

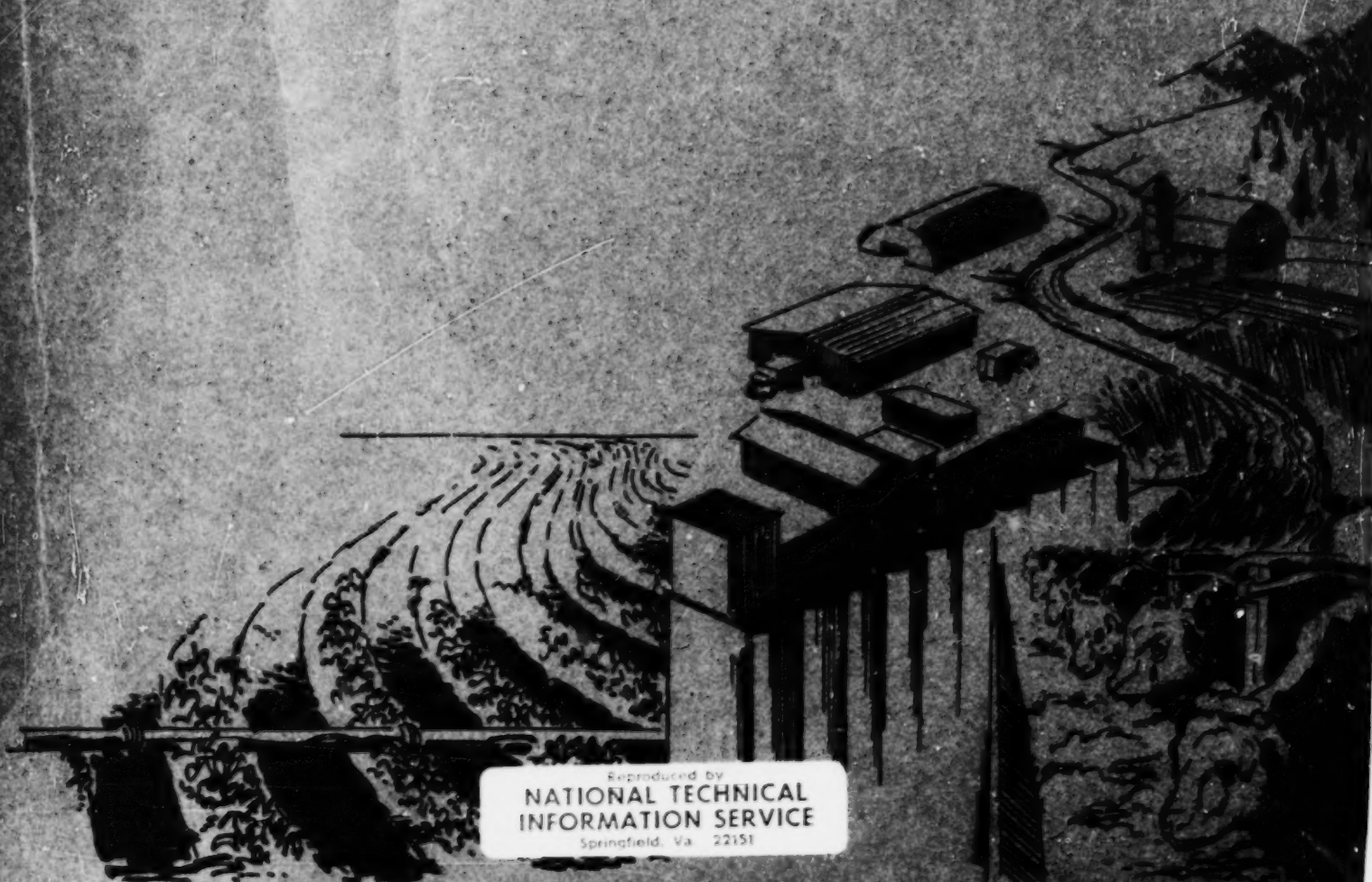


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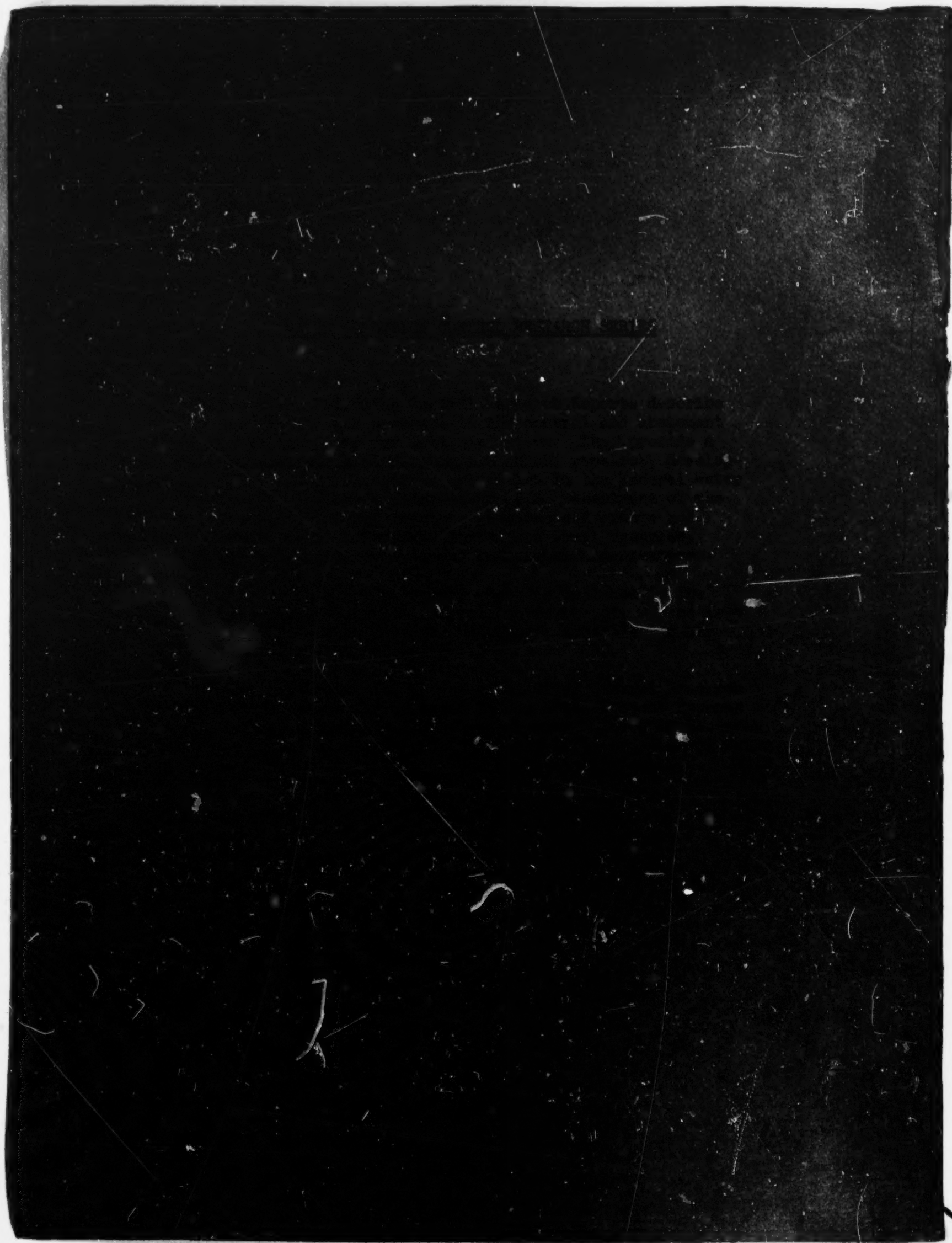
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COLLECTED PAPERS REGARDING NITRATES IN AGRICULTURAL WASTE WATER



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27 Abstract This is a collection of 11 papers dealing with the closely related topics of (a) concentrations of nitrates occurring in subsurface agricultural waste waters, (b) the source of nitrates, and (c) possible methods for controlling or removing them. The work all deals with subsurface agricultural waste waters of the San Joaquin Valley in California, but much of the information may have general application. <i>(See also W71-04547 thru W71-04557)</i> <i>(WRSIC abstract)</i> <i>(Knapp. U SGS)</i>		
Abstractor George Knapp 1-31-70	Institution U. S. Geological Survey, Water Resources Division	

Collected Papers
Regarding Nitrates
In
Agricultural Waste Waters

Compiled By
The
Federal Water Quality Administration
760 Market Street, San Francisco, California 94102

The
United States Bureau of Reclamation
2800 Cottage Way, Sacramento, California 95825

and The
California Department of Water Resources
1416 Ninth Street, Sacramento, California 95814

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FOREWORD

This is a collection of individual papers dealing with the closely related topics of (a) concentrations of nitrates occurring in subsurface agricultural waste waters, (b) the source of nitrates, and (c) possible methods for controlling or removing them. The work reported herein all deals with subsurface agricultural waste waters of the San Joaquin Valley in California, but much of the information may have general application. The papers all were prepared for, and presented originally at, the National Fall Meeting of the American Geophysical Union on December 16, 1969, in San Francisco. Since that time a few revisions have been made by the authors, who are solely responsible for the contents, but no editing was done in connection with publication of the papers as a collection.

In the interval between preparation of the papers and printing of this collection, the Federal Water Pollution Control Administration has shortened its name to Federal Water Quality Administration.

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GENESIS AND SCOPE OF
INTERAGENCY COOPERATIVE STUDIES OF
CONTROL OF NITRATES IN
SUBSURFACE AGRICULTURAL WASTE WATERS

By

Edgar P. Price¹

Introduction

The program of the United States Bureau of Reclamation to construct San Luis Drain, the plans of the California Department of Water Resources to construct a San Joaquin Valley master drain, and the concern of these two agencies and that of the Federal Water Pollution Control Administration for water quality in San Francisco Bay prompted the three agencies in 1967 to launch a cooperative investigation of methods for removing nitrates from subsurface agricultural waste water. The investigation soon broadened technically and organizationally to include examination of the source of the nitrates and the changes in nitrate form which might occur spontaneously or which might be induced as the subsurface water is collected and conveyed through California's San Joaquin Valley to the head of the San Francisco Bay System.

In addition to the three agencies already mentioned, parts of the overall investigation are being conducted or supported by the Agricultural Research Service, the Soil Conservation Service, the Office of Saline Water, the University of Arizona, and the University of California at Davis. Faculty members from both Stanford University and the University of California at Berkeley are serving as consultants. Other governmental organizations, educational institutions, and private firms are performing services or doing related work. The cost of the program will be approximately \$3 million, most of which will be spent during the 3-year period 1967-70. Some parts of the research will continue past 1970. The results will be generally applicable in most, if not all, irrigated areas which dispose of their subsurface agricultural waste waters to a water body, either surface or underground.

This paper gives the background and an overview of the entire investigation. The several other related papers which follow give detailed information about specific experiments.

¹ U.S. Bureau of Reclamation, Sacramento, California

Drainage Problem of the San Joaquin Valley

It was the saline water drainage problem of the San Joaquin Valley which drew both the Department of Water Resources and the Bureau of Reclamation into the interagency cooperative waste water treatment study. For over a century, irrigated agriculture has been expanding in the San Joaquin Valley which, as illustrated on figure 1, forms the southern portion of California's Central Valley. This growth has been paralleled by a rising concern over the problems of drainage; not merely the problem of keeping excess water out of crop root zones but of protecting the sources of irrigation water, both surface streams and ground water, from harmful concentrations of salt contributed by agricultural return flows. For years, irrigators have sought an alternative to the San Joaquin River as a drainage outlet to remove salts from the almost completely enclosed San Joaquin Valley. Aided by studies of the California Department of Water Resources and the United States Bureau of Reclamation, the irrigators' efforts were rewarded in 1960. In that year Congress authorized construction of facilities to import additional water to the 500,000-acre San Luis Unit service area on the west side of the San Joaquin Valley and included provision for construction of a canal (San Luis Drain) to convey drainage waters back to the western Sacramento-San Joaquin Delta near Antioch. These features are shown on figure 2. At about the same time the voters of California approved the long-range State Water Plan which incorporated a proposed master drain to dispose of saline waters from all portions of the San Joaquin Valley which might require such service.

The proposed State and Federal drainage facilities were not intended to be competitive; the Federal Drain was to serve only the San Luis Unit service area and was to be built only if the State's master drain did not materialize. After independent studies of many possible solutions, both agencies decided upon conveyance of the saline waters to a point near the city of Antioch where they believed the saline drain waters could be discharged without significantly increasing the salinity of the receiving waters. The bases for selecting this plan are recorded in a report entitled "San Joaquin Master Drain" (1)² issued by the Department of Water Resources and a report entitled "Alternative Solutions For Drainage" (2) issued by the Bureau of Reclamation.

Beginning in 1964, the Department of Water Resources and the Bureau of Reclamation cooperated diligently in an attempt to bring about construction of a master drain by the Department to which the Bureau would contribute financially in return for

² Parenthetical numbers refer to literature cited.



Figure 1, Location Map

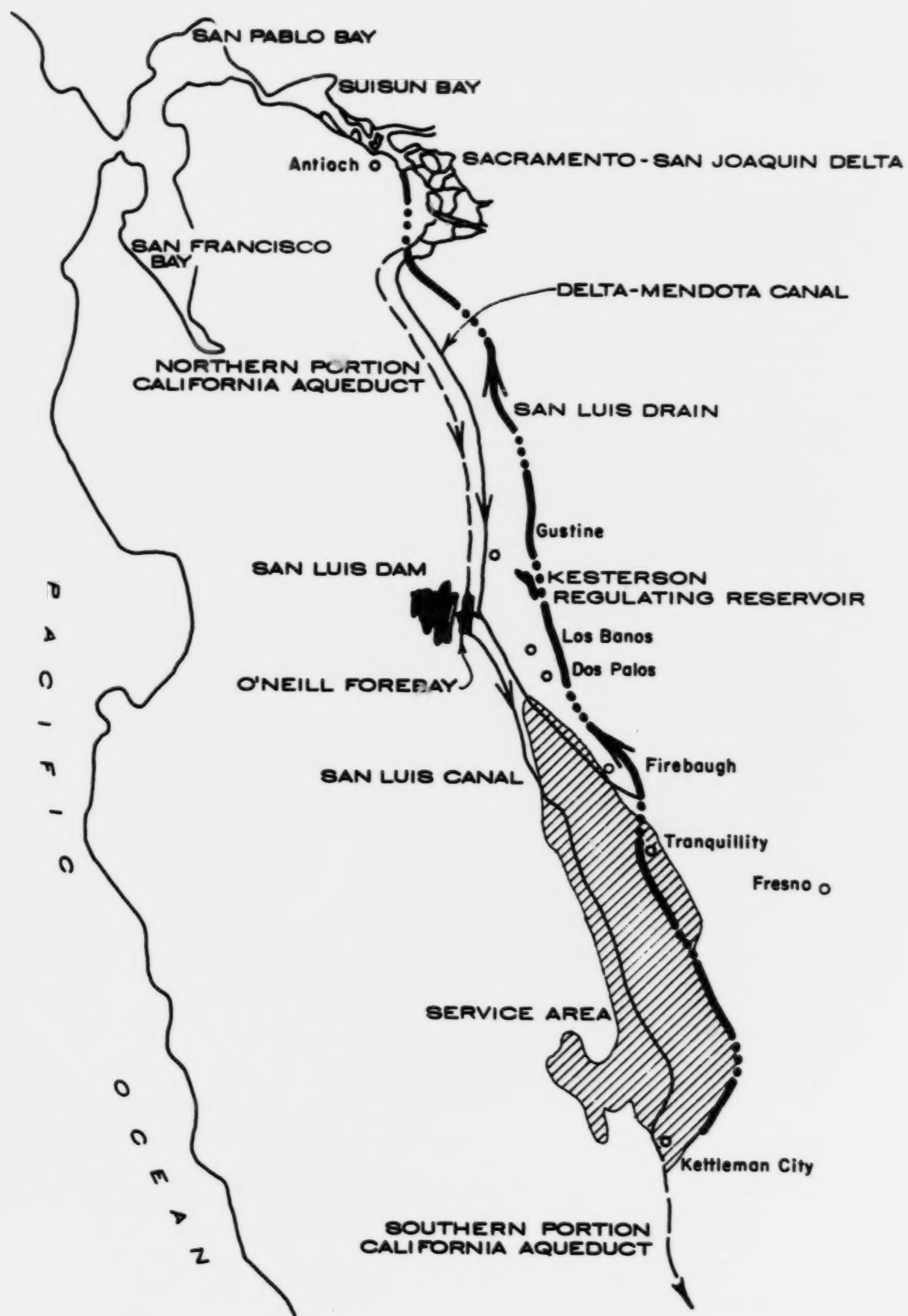


Figure 2. San Luis Unit and Related Facilities

drainage disposal service for the Federal San Luis Unit. During this period the Department recognized the need to study ways of removing nitrates from the drainage waters and in 1965 began negotiations to secure a research grant from the Federal Water Pollution Control Administration. At this time the Bureau of Reclamation was expecting to contribute financially to the research effort as part of its share of the cost of the master drain but not to participate actively. In early 1967, however, the picture changed drastically when the Department decided to defer construction of a master drain indefinitely because of the unwillingness of many local agencies in the San Joaquin Valley to contract for drainage disposal service. The Bureau then began constructing San Luis Drain and, as a corollary thereto, preparing itself to cope with nitrates in the drain waters if these substances were to prove deleterious. Since the Department still expected to someday construct and operate a drainage facility in the San Joaquin Valley it wished to pursue the nitrate research program it had set in motion.

San Luis Drain

San Luis Drain, which the Bureau of Reclamation now is constructing in the San Joaquin Valley, will be a concrete-lined canal extending 188 miles northward from near Kettleman City to the western edge of the Delta near Antioch. About two-thirds of the way from Kettleman City to Antioch, near Gustine, a regulating reservoir called Kesterson Regulating Reservoir will be constructed as an integral part of the drain.

The drain throughout its length will be hydraulically isolated from all surface and ground water so that it will neither contribute water to, nor receive water from, any surface channel or ground-water body it crosses. The water flowing in San Luis Drain will be subsurface agricultural waste water received under contract and discharged from drainage collector systems.

The capacity of San Luis Drain will increase from 100 c.f.s. at its southern beginning to 300 c.f.s. at its entrance to Kesterson. From Kesterson to Antioch the capacity of the drain will be a uniform 450 c.f.s. Kesterson Reservoir will function initially as a simple holding pond in which the early flows reaching San Luis Drain will be held until construction of the northern portion of the drain is complete and discharge to the upper end of the San Francisco Bay system begins. Using Kesterson Reservoir in this manner will permit drainage of land to start soon but will allow an extra year or two in which to complete the nitrate control research program before discharge near Antioch begins.

In 1967, when the research program was initiated, the construction of San Luis Drain was scheduled as a three-step process: Firstly, 65 miles of the drain from Tranquillity to Kesterson Reservoir and a portion of the reservoir were to be completed by December 1969; secondly, the southernmost segment of the drain between Tranquillity and Kettleman City was to be completed by December 1970; and lastly, the remainder of Kesterson Reservoir and the drain from the reservoir to Antioch were to be completed by December 1971. This was the construction schedule to which the research schedule was geared. Reductions in Federal appropriations have forced delays of 2 years or more in all phases of San Luis Drain construction, but the research program has been kept on schedule and conclusions will be available in 1970.

Protecting San Francisco Bay

The Federal Water Pollution Control Administration is interested in the interagency cooperative study of the role of nitrates in subsurface agricultural waste water as a means of protecting the quality of water throughout the San Francisco Bay system and the Sacramento-San Joaquin Delta. In 1962 the Bureau asked the Administration (then a part of the Public Health Service) to look into the subject. In addition, local interests in the Bay Area opposed the drainage plans of the Bureau and the Department, and these agencies urged that a study be made of the possible effects on water quality. The opponents maintained that such drainage discharge would: (a) usurp assimilative capacity of the Bay system which properly should be reserved for the individual and corporate residents immediately adjacent to San Francisco Bay; (b) significantly increase the salinity of the receiving waters in the vicinity of Antioch thereby further shortening the intermittent periods when such waters now are suitable for municipal, industrial, or agricultural use; (c) compound the problem of pesticides, and (d) accelerate catastrophically the eutrophication of the Bay-Delta estuarine combination.

In response to these requests for study and allegations of damages, the Federal Water Pollution Control Administration undertook a comprehensive study of the probable effect of the San Joaquin Valley Master Drain on San Francisco Bay and in January 1967 published its report (3). Essentially, the report concluded that the fears related to assimilative capacity, salinity, and pesticides were greatly exaggerated but that the anticipated nitrate content of the drain waters might produce extensive algal blooms in the receiving waters. One of the principal recommendations of the Federal Water Pollution Control Administration, therefore, was that a feasible method of nitrate removal be worked out before any agricultural drainage discharge to the Bay system be allowed. The

Administration estimated that 3 years of research would be required to select a removal method from amongst several which had shown promise on a laboratory scale and to design a practical facility capable of removing nitrates under field conditions.

Quantity and Quality of San Joaquin Valley Drainage

The most recently compiled estimates of the quantities of subsurface agricultural waste water which will have to be disposed of from the San Joaquin Valley are given in table 1. These estimates were issued by the San Joaquin Valley Drainage Advisory Group (4) composed of individuals drawn from organizations engaged in water management in all parts of the San Joaquin Valley. The table basically is a combination of estimates made by the Department of Water Resources and the Bureau of Reclamation. The range of dates indicates that such estimates involve a large measure of judgment. The year-to-year increase in subsurface agricultural waste water entering a drainage disposal system depends upon how and when individual irrigators install tile drainage as well as upon when and where they begin application of the additional irrigation water supplies made available by the major State and Federal water importation projects. Some information on the status and prospects of tile drain installations in the San Joaquin Valley has been reported by the Soil Conservation Service (5) and by William R. Johnston (6), the drainage expert on the staff of Westlands Water District located in the Federal San Luis Unit service area.

Table 2 shows the concentrations of various substances which are anticipated for the drainage water which will flow in San Luis Drain. These probably are reasonably representative of the concentrations which will occur in discharges from any drainage disposal facility serving other areas of the San Joaquin Valley, too. The initial concentrations of all salts are higher than those anticipated 50 years hence. This is because there exist accumulations of these salts which will be removed by draining away the shallow ground water and leaching the soils. Afterwards the concentrations of salts in the drainage effluents should be just sufficient to make the rate of disposal equal to the rate of input for each salt. Those substances for which no change in concentration is anticipated either have not been accumulating or else accumulations of them cannot be removed by draining and leaching.

The macronutrients, nitrogen and phosphorous, of course, are the substances of primary interest when considering eutrophication. The Federal Water Pollution Control Administration in its

Table 1. Estimated annual agricultural
waste water disposal requirement

Year ¹	Annual Requirement (1,000 A/F)			Total
	San Luis Unit ²	:	Other parts of Valley ³	
1970, 1975	5		82	87
1980, 1990	53		200	253
1990, 2005	123		318	441
2000, 2020	155		401	556
2010, 2035	162		414	576
2020, 2050	162		421	583

- ¹ Earliest and latest estimated dates.
² USBR estimate.
³ DWR estimate.

Table 2. Estimated concentrations
of chemical substances in
San Luis Drain waters

<u>Substance</u>	<u>1970 Conditions mg./l.</u>	<u>2020 Conditions mg./l.</u>
Total dissolved solids	7,000	3,000
Salts		
Sulfate	3,000	700
Sodium	1,500	700
Chloride	1,200	900
Calcium	300	100
Magnesium	200	50
Bicarbonate	200	100
Potassium	20	10
Boron	10	3
Nutrients		
Total Nitrogen	20	20
Total Phosphate	0.15	0.15
Pesticides	<0.001	<0.001

previously cited report on the effect of the San Joaquin Master Drain identified nitrogen as the limiting nutrient in the case of San Francisco Bay and estimated the maximum safe concentration of nitrogen as 2.0 milligrams per liter if unacceptable algae blooms are to be avoided in the Bay and Delta waters. This has been adopted as the goal of the interagency cooperative program for nitrate control or removal, and it means that methods must be developed to reduce the nitrogen concentrations in the drainage waters by 90 percent.

The latest comprehensive study of the Bay System's water quality problems and possible control methods (7) states that neither nitrogen nor phosphorus is growth limiting in San Francisco Bay and the Delta. Furthermore, the report indicates that even without any nitrate removal the subsurface agricultural waste water from San Luis Drain would be less than one-half of one percent of the total nitrogen loading in the Bay. The report postulates that unspecified biostimulants, if not controlled or eliminated, will result in undesirable eutrophication. This, apparently, indicates a need to search for biostimulants rather than nitrogen removal methods. However, since the biostimulants have not been identified and the concept is general, the growth-limiting factor in San Francisco Bay may not be the absence of a biostimulant but the presence of a biodepressant (a negative biostimulant). This might be a toxic substance coming from municipal and industrial waste discharges or the turbidity of the waters.

The contrast between the view of one agency that nitrogen is growth-limiting in San Francisco Bay and the view of another agency that it is not, simply confirms that the conclusion of Professor Charles M. Weiss (8) regarding lakes and reservoirs also applies to the San Francisco Bay estuarine system: "The rate of trophic response of each lake or reservoir to changes in macronutrient levels involves not only nutrient change, but also the total chemical and physical characteristics of the particular basin."

In view of the uncertainties surrounding the eutrophic process generally and eutrophication in San Francisco Bay in particular, the nitrogen control and removal experiments have and will be continued. They may or may not be applicable to San Joaquin Valley subsurface agricultural drainage discharges but whoever operates a facility making such a discharge to San Francisco Bay should be prepared to institute procedures to control nitrogen levels if necessary. Furthermore, such removal or control methods may have utility elsewhere even if never needed in connection with San Francisco Bay.

Research Program Formulation

From December 1963 on, the California Department of Water Resources had been studying algae stripping as a promising process for removing nitrates from drainage water. In the course of this effort the Department made application to the Federal Water Pollution Control Administration for a financial grant and also had requested the use of some land owned by the United States along the Delta-Mendota Canal of the Bureau of Reclamation for construction of an experimental facility. The site, near Firebaugh, was selected because it was adjacent to a drain sump receiving water from tile drain lines underlying approximately 400 acres of farmland typical of the lands in the San Joaquin Valley through which ultimately will need drainage to remain in agricultural production. The owners of the land had agreed to let the Department of Water Resources divert as much of the subsurface agricultural waste water as would be needed for experiments. In early 1967, the Department of Water Resources announced deferment of construction of a San Joaquin Valley Master Drain and thus set in motion the program of the Bureau of Reclamation to construct San Luis Drain. Another result of this switch in construction agencies was to alter the role of the Bureau of Reclamation in the nutrient research program from that of a financial supporter to that of an active participant. This was necessary, of course, because Bureau personnel would be operating and maintaining San Luis Drain and whatever treatment facilities may prove to be necessary.

In January 1967 the three agencies met to lay out the research program and synchronize the research and drain construction programs. There was unanimous agreement on the importance of the work, and there was quick agreement to implement the research program which the Department of Water Resources had planned for the Firebaugh site. A contract was signed by the three parties calling for a 3-year program of research into the removal of nitrates by the algae-stripping method (sometimes called the biomass production and harvesting method)--that is, the forcing of maximum growth of algae in drain water held in special ponds followed by separation of the algae from the water. The contract also specified that a quick evaluation would be made of the potentialities of biological denitrification--a term which refers to the reduction of nitrates by bacterial action in anaerobic conditions.

The meeting in January 1967 to establish the research program was characterized by an eagerness on the part of all involved agencies to go the extra mile. As a result, the individual agencies were suggesting additional and related experiments which they alone or in combination with some fourth agency, would finance and conduct. The Federal Water Pollution Control Administration in cooperation

with the Office of Saline Water decided to test desalting units on the San Joaquin Valley's brackish water, and they chose a reverse osmosis unit and an electro-dialysis unit for this purpose. The Bureau of Reclamation contracted with the Universities of California (Davis) and Arizona to develop a digital computer program modeling the nitrogen transformations which take place in the soil-water systems and to verify the model with a series of field plot and lysimeter experiments. Both the Federal Water Pollution Control Administration and the Bureau of Reclamation contracted with private concerns for pilot research on resins which might selectively reject the nitrate ion. The Department of Water Resources continued its program of sampling drainage sumps in many parts of the San Joaquin Valley, and the Federal Water Pollution Control Administration instituted intensive sampling of a limited number of selected drain sumps. The Federal Water Pollution Control Administration also financed a pilot study of denitrification in sulfur columns at the California Institute of Technology. This was the scope of the comprehensive program which the three agencies put down on paper in January 1967 and which was well underway 6 months later.

In subsequent months the Federal Water Pollution Control Administration greatly expanded the biological denitrification experiments at the Firebaugh site because of the promise the method showed. Also, the Bureau of Reclamation, the Agricultural Research Service, and the Soil Conservation Service in cooperation with a local valley farmer began an experiment to see if a useful degree of biologic denitrification could be achieved right in the soil of the irrigated fields simply by designing and installing tile drains which would be submerged and therefore anaerobic at all times.

Conclusion

The individual experiments have produced much information, and a lot of it is recorded in the other 11 selected papers which follow. As yet, no attempt has been made to reach conclusions regarding the overall control of nitrates in the subsurface agricultural waste waters of the San Joaquin Valley. This will come in the next few months after most of the experiments are completed and the results fully assessed.

From the viewpoint of those engaged in the development and protection of natural resources, however, the evolution and execution of a program of this sort is significant. In this day and age, dealing with natural resources inevitably involves coping with an increasing complexity of inter-related causes and effects; integrating work from an increasing number of scientific specialities;

keeping abreast of an increasing array of technical problem-solving tools and techniques; and last, but certainly not least, dealing with a rapidly-growing number of organizations. This program is one example of how this may be approached.

From the viewpoint of a manager in natural resources development the aspects to be emphasized are:

(a) The comprehensive nature of the experimental program which aims to determine not only how nitrates can be removed most economically from subsurface agricultural waste water but where the nitrates originate, what transformations they undergo in the soils, in the drain canal, and in holding ponds; and what possibilities exist for influencing the sources and the transformations in order to reduce--or perhaps even eliminate--the need for extensive facilities solely to remove nitrates.

(b) The effective way in which a wide range of private citizens, governmental agencies, universities, and people--from individual farmers to scientific consultants--are bringing their knowledge, experience, and other resources to bear on this problem of controlling nitrates in subsurface agricultural waste water. About every 6 months a meeting is held to review progress on all experiments and exchange data; in between these meetings there are many smaller meetings, and of course, the fact that many of the experiments are located at the interagency Firebaugh site guarantees a high degree of cross-fertilization of ideas.

(c) The cooperative nature of the program which will cost in the neighborhood of \$3 million over a 3-year period from 1967-70. About one-third of this amount is involved in the three-party contract involving the Department of Water Resources, the Federal Water Pollution Control Administration, and the Bureau of Reclamation. The other two-thirds of the program is administered by the individual agencies but in such a manner as to make a timely and significant contribution to the comprehensive program.

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PREDICTING CHANGES IN NITROGENOUS COMPOUNDS IN SOIL-WATER SYSTEMS

By

Marvin J. Shaffer, Gordon R. Dutt,
and William J. Moore¹

Introduction

A digital computer program was developed which models soil-water systems with respect to nitrogen transformations, including hydrolysis of urea, immobilization-mineralization of ammonia and organic nitrogen, and immobilization of nitrate nitrogen. Transformation rate equations were derived by applying techniques of systems and statistical analysis and using selected data from the literature. Simultaneous integration of the equations over time generates predicted concentrations for urea-N, organic-N, ammonia-N, and nitrate-N in the system. Comparisons were made of predicted and observed data for several soils having different textures and various moisture contents, temperatures, and fertilizer applications. This procedure yielded simple correlation coefficients of 0.99, 0.97, and 0.97 for the previously mentioned nitrogenous types, respectively.

Nitrogen is an important component of most soil-water systems. It is involved in a variety of biochemical and physical processes occurring in soils. Excessive accumulations or deficiencies of one or more nitrogenous species may lead to high nitrogen concentrations in agricultural drainage waters and nitrogen deficiencies or excessive foliar growth of plants. A model predicting the concentrations of nitrogenous species occurring in soil-water systems would aid in planning management criteria for pollution control and fertilizer programs. This study was concerned with the development of a digital computer model based on data available in the literature, to serve as part of a more comprehensive model for soils.

Methods and Theory

To simplify the investigation discussed above, the soil-water system was restricted in several aspects. Leaching and plant uptake of

¹ Graduate Associate, Professor, and Graduate Associate, respectively. University of Arizona, Tucson, Arizona. This research was supported in part by the U.S. Bureau of Reclamation contract 19-06-D-6464. Arizona Agr. Exp. Sta. Technical Paper.

nitrogen were neither considered nor allowed in the model. The assumption was made that denitrification is not a significant process in the system as defined (9).³ To eliminate many acid soil reactions, only alkaline soils were considered. Further, it was assumed that nitrogen and ammonium fixation and nitrite concentration are negligible.

The basic nitrogen transformation pathways considered in this model are illustrated in figure 1. The peripheral arrows represent inputs to the model. Urea hydrolysis denotes the conversion of urea to ammonia nitrogen. The mineralization-immobilization pathway accounts for the net conversion of ammonia to organic nitrogen or organic to ammonia nitrogen. Nitrification represents the net production of nitrate from ammonia nitrogen. Net reduction of nitrate to ammonia nitrogen probably would not occur in this restricted system. Immobilization of nitrate nitrogen is described by the nitrate-N pathway.

These pathways designate nitrogen transformations in the model system. Modification of this system could allow incorporation of additional pathways.

The basic inputs and outputs of the model are illustrated in figure 2. Initial soil conditions with respect to concentrations of nitrogenous species, temperature, moisture, and carbon to nitrogen ratio represent one set of inputs. Others include additions of urea, ammonia, organic, and nitrate nitrogen with time. Moisture and temperature changes with time were allowed. Concentrations of the nitrogenous species in the system with time were considered as outputs from the model.

Experimental data needed to develop mathematical relationships for the transformation pathways were obtained from the literature. Data suitable for the urea hydrolysis pathway were obtained from papers by Broadbent, Hill, and Tyler (4), and Overrein and Moe (8). Work by Broadbent (2 and 3) and Alexander (1) provided data for the mineralization-immobilization pathway. Nitrification data were obtained from Broadbent, Tyler, and Hill (5), and Justice and Smith (7). Finally, work by Broadbent (3) provided nitrate immobilization data.

Since nitrogen transformations usually proceed at a slow rate, equilibrium considerations used in earlier models, e.g. (6), were

³ Parenthetical numbers refer to literature cited.

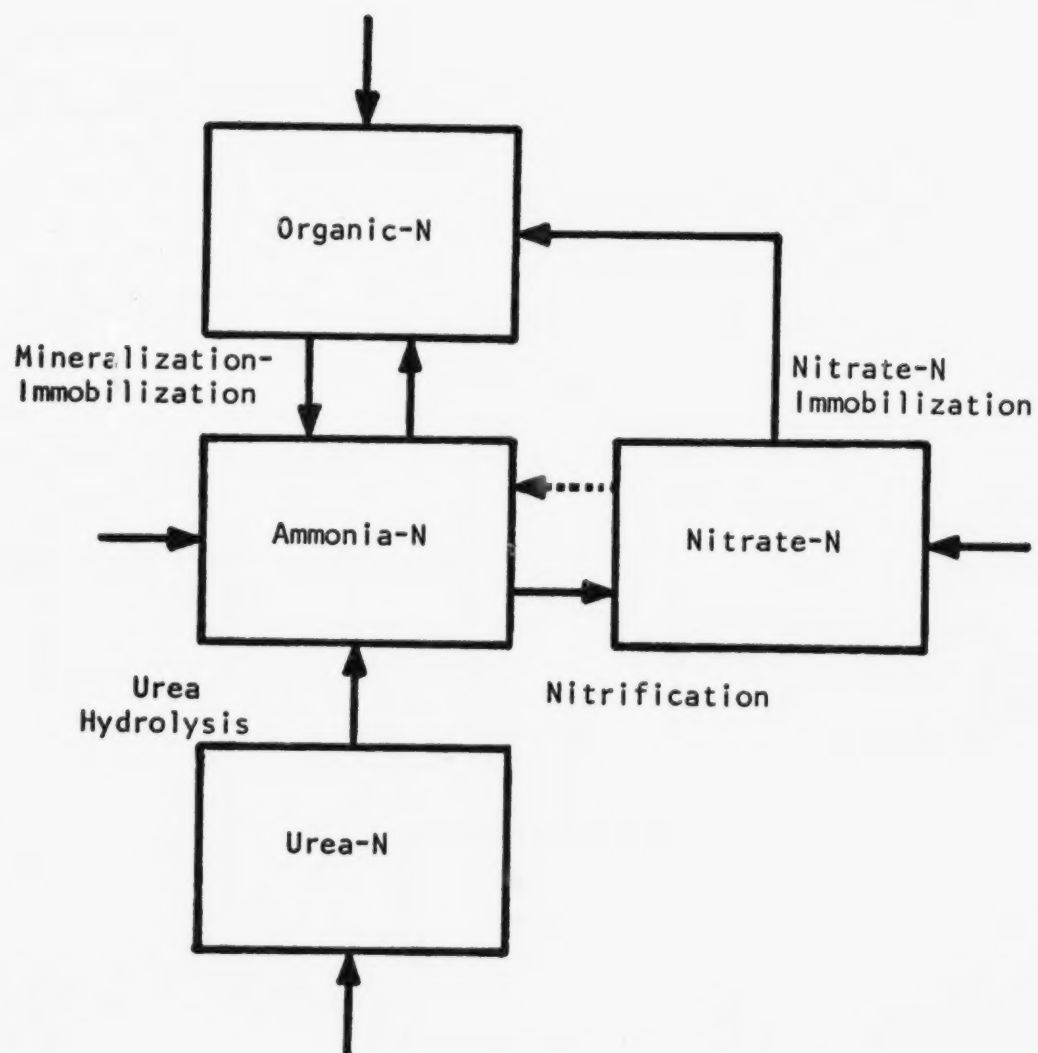


Fig. 1. Biochemical and Chemical Pathways Within the System Model

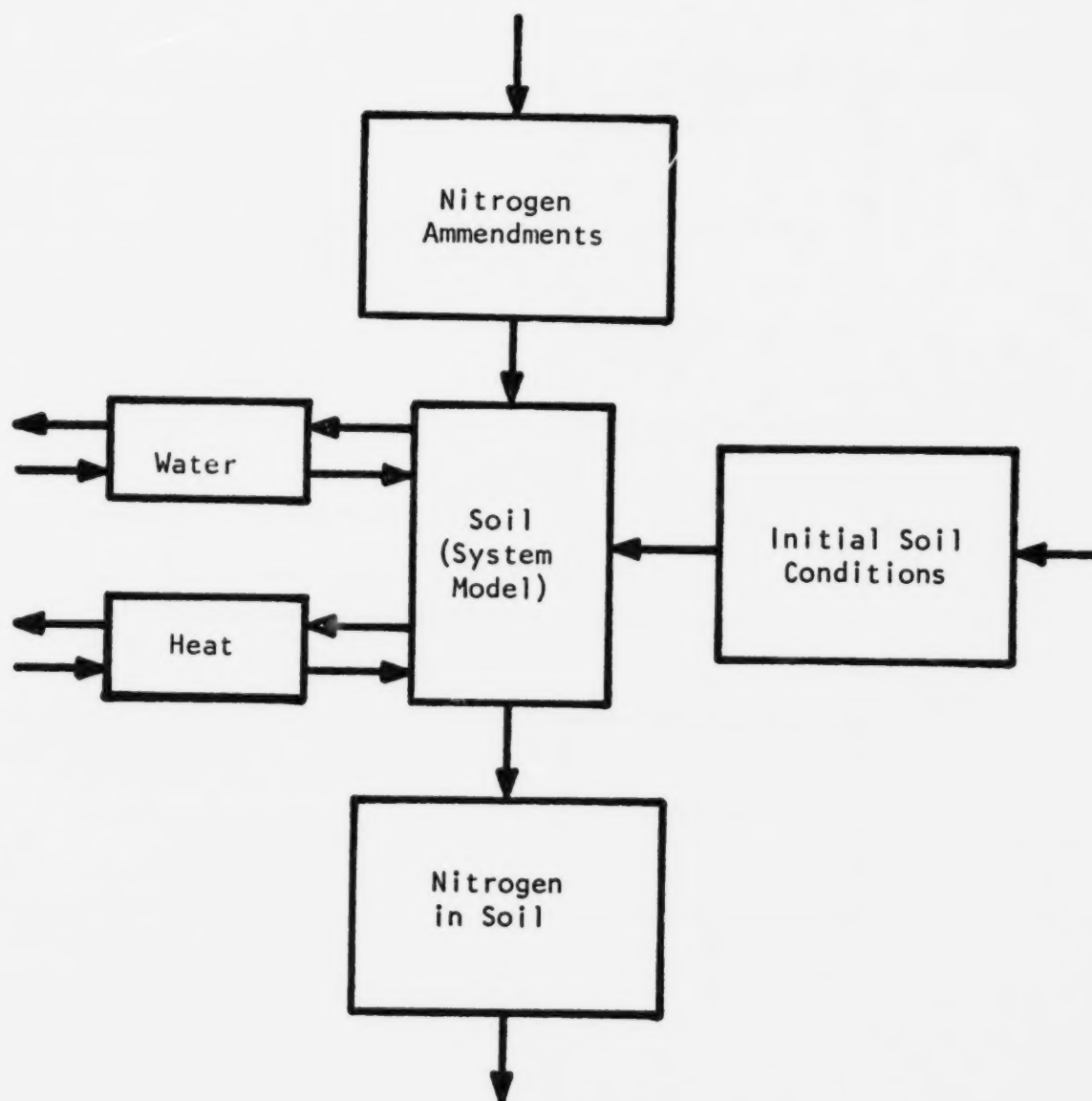


Fig. 2. Basic Inputs and Outputs of the System Model

abandoned in favor of a kinetic approach. Attempts were made to derive transformation rate equations for each pathway as a function of the variables indicated below.

$$\text{Rate} = f(\text{concentrations of urea-N, NH}_3\text{-N, organic-N, and NO}_3\text{-N; temperature; moisture; C:N ratio; texture; pH})$$

This procedure was simplified by applying computerized multiple linear regression techniques. In general, the form of each rate equation was as follows:

$$R = C + b_1x_1 + b_2x_2 + \dots b_nx_n$$

Where R is rate (dependent variable).

C is a constant (Y-intercept).

x_n is an independent variable.

b_n is a constant (regression coefficient).

Various combinations of independent variables were tried to obtain the best fit as evidenced by the multiple correlation coefficient and F ratio. Only those variables or variable combinations making significant contributions to the regressions were included in the final equations. The primary objective was to obtain equations describing the effects of the independent variables and account for their interactions.

At this point, it is well to note that at temperatures less than 10° C. and/or nitrogen concentrations below 10 p.p.m., exponential rate functions were used to adjust the output of the regression rate equations. This procedure yielded better data fits near these boundaries. Similarly, exponential moisture functions were included to correct the regression equations for moisture contents below 10 bars tension. Moisture content was not found to be a significant variable above this tension. Also, an expression including C:N ratio, derived from work done by Alexander (1) and Broadbent (2), adjusted the output of the mineralization-immobilization regression equations for changes in C:N ratio of the organic residue. A summary of the final regression equations and statistical tests appears in table 1 and table 2.

Next, it was necessary to solve the equations simultaneously to obtain changes in nitrogen concentrations in the model. For a given time interval, the same initial conditions were utilized by each rate equation. The computed changes in concentration from each equation were used to determine the initial concentrations for the next interval. Predicted nitrogen concentrations with time were approximated by successively increasing the number of time intervals included between times T_1 and T_2 ($T_2 - T_1 = 1$ day) and repeating the

Table 1. Variables, Constants, and Statistical Tests for the Urea Hydrolysis and Mineralization-Immobilization Rate Equations.

Equation	Urea Hydrolysis	Mineralization-Immobilization
Variable:	$\log_{10} T$	T
r Value:*	$6.22 \cdot 10^{-1}$	$-5.85 \cdot 10^{-1}$
Coefficient (b1):	$-1.56 \cdot 10^2$	$-2.16 \cdot 10^{-3}$
Variable:	$\log_{10} \text{urea-N}$	organic-N
r Value:	$6.78 \cdot 10^{-1}$	$-7.69 \cdot 10^{-1}$
Coefficient (b2):	$-1.53 \cdot 10^2$	$-2.70 \cdot 10^{-2}$
Variable:	—	$\log_{10} \text{ammonia-N}$
r Value:	—	$7.06 \cdot 10^{-1}$
Coefficient (b3):	—	$3.92 \cdot 10^{-1}$
Constant:	$4.13 \cdot 10^2$	$8.92 \cdot 10^{-1}$
F Ratio:	$6.24 \cdot 10^1$	$3.89 \cdot 10^1$
R ² Value:**	$7.23 \cdot 10^{-1}$	$7.40 \cdot 10^{-1}$
SEE:***	$4.90 \cdot 10^1$	$2.45 \cdot 10^{-1}$

* Simple Correlation Coefficient

** Multiple Correlation Coefficient Squared

*** Standard Error of Estimate for the Rate

Table 2. Variables, Constants, and Statistical Tests for the Nitrification and Nitrate-N Immobilization Rate Equations.

Equation	Nitrification	Nitrate-N Immobilization
Variable:	T x (ammonia-N)	T/(organic-N) ²
r Value:	5.44·10 ⁻¹	4.18·10 ⁻¹
Coefficient (b1):	1.62·10 ⁻³	1.52·10 ⁰
Variable:	log ₁₀ ammonia-N	e ^T
r Value:	3.61·10 ⁻¹	-2.82·10 ⁻¹
Coefficient (b2):	2.38·10 ⁻¹	-3.23·10 ⁻¹⁵
Variable:	log ₁₀ nitrate-N	(T x (organic-N) - (nitrate-N))/(organic-N)
r Value:	-4.97·10 ⁻¹	3.24·10 ⁻¹
Coefficient (b3):	-2.51·10 ⁰	-4.90·10 ⁻³
Constant:	4.64·10 ⁰	0.0
F Ratio:	2.91·10 ¹	9.96·10 ⁰
R ² Value:	3.84·10 ⁻¹	4.21·10 ⁻¹
SEE:	3.67·10 ⁰	4.11·10 ⁻¹

calculations. This process was continued until the concentration of each nitrogenous species at T_2 agreed to within 0.5 p.p.m. of its previous value. That is, the system converged. A generalized block diagram of the computer program illustrating the method of solving the equations appears in figure 3.

Next, the predicted nitrogen concentrations were compared with the observed data used to derive the rate equations. Adjustments in certain coefficients were necessary to improve the fit in the assembled model. Interactions between the independently derived rate equations could account for the corrections needed. A summary of changes made in coefficients appears in table 3.

Discussion of Results

Techniques of data pairing were employed to test the reliability of the model. Sets of observed and predicted values for each nitrogenous species studied were compared by using a least squares linear regression analysis to obtain the simple correlation coefficient, the regression coefficient, the Y-intercept, and the standard error of estimate. This observed data was a combination of data used to derive the model together with all other available data applicable to the model. Results of this analysis for each of the four nitrogenous types studied are given in table 4. Data obtained from duplicate runs were omitted to avoid inclusion of many similar points. Data represented results from several different soil series and types. The lower correlation coefficient for organic nitrogen may have been due to the relatively narrow data range considered.

Typical observed and predicted curves for urea, organic, ammonia, and nitrate nitrogen concentrations versus time are given in figures 4, 5, 6, and 7. Some runs gave better agreement, while others did not agree as well. This model can be used to predict changes in concentrations of nitrogenous species in soil-water systems undergoing incubation. Of more importance is its potential application to dynamic soil-water systems of practical interest. Such a model is currently under development.

Summary

The objective of this research was the development of a digital computer model predicting nitrogen concentrations in soil-water systems. The system was restricted by certain assumptions and limitations. After establishing primary pathways for nitrogen transformations, corresponding mathematical equations were derived using a statistical analysis of data from the literature. These equations were combined and solved in a computer program which became the basic model. The model was verified by comparing its predicted output with observed data from the literature.

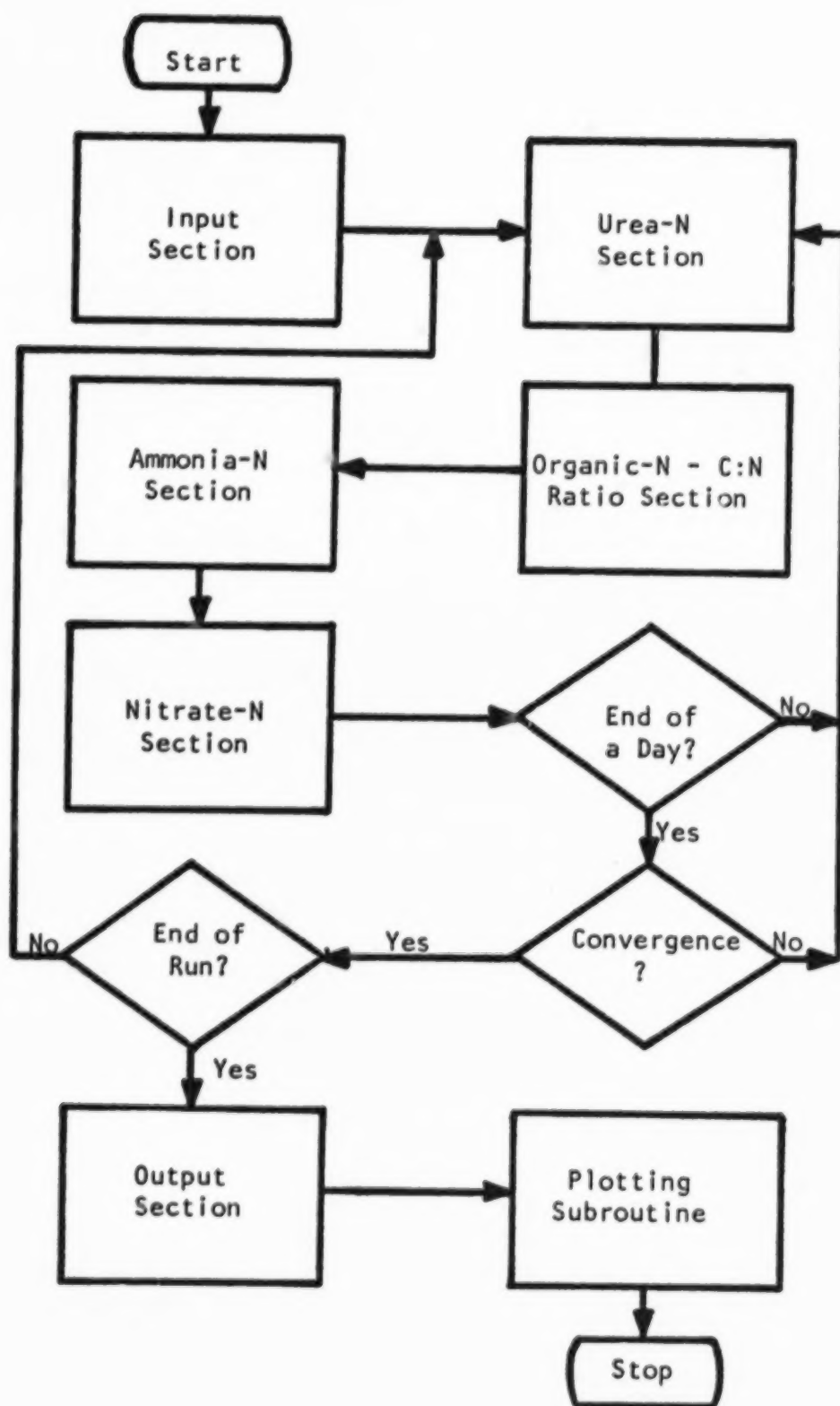


Fig. 3. Generalized Block Diagram of the Computer Program

Table 3. Summary of Corrections Made in Regression Coefficients

Equation	C:N Ratio	b1	b2	b3
Urea Hydrolysis	—	NC*	NC	—
Mineralization- Immobilization	< 23	NC	NC	$1.60 \cdot 10^0$
	≥ 23	NC	NC	$7.83 \cdot 10^{-1}$
Nitrification	< 23	NC	$4.50 \cdot 10^0$	NC
	≥ 23	$8.00 \cdot 10^{-4}$	$2.38 \cdot 10^{-4}$	$-2.10 \cdot 10^0$
Nitrate-N Immobilization	< 23	NC	NC	NC
	≥ 23	NC	NC	NC

* NC = No Change.

TABLE 4

RESULTS OF PAIRING PREDICTED AND OBSERVED DATA

NITROGEN SPECIES: UREA-N ORGANIC-N AMMONIA-N NITRATE-N			
NO. OF PAIRS:	31	56	83
% NEW DATA:	0	0	50
DATA RANGE:	0-400	15-60	0-150
(PPM)			
r VALUE	0.992	0.774	0.969
SEE:	17.1	6.55	9.47
SLOPE:	0.925	0.768	1.05
			0.884

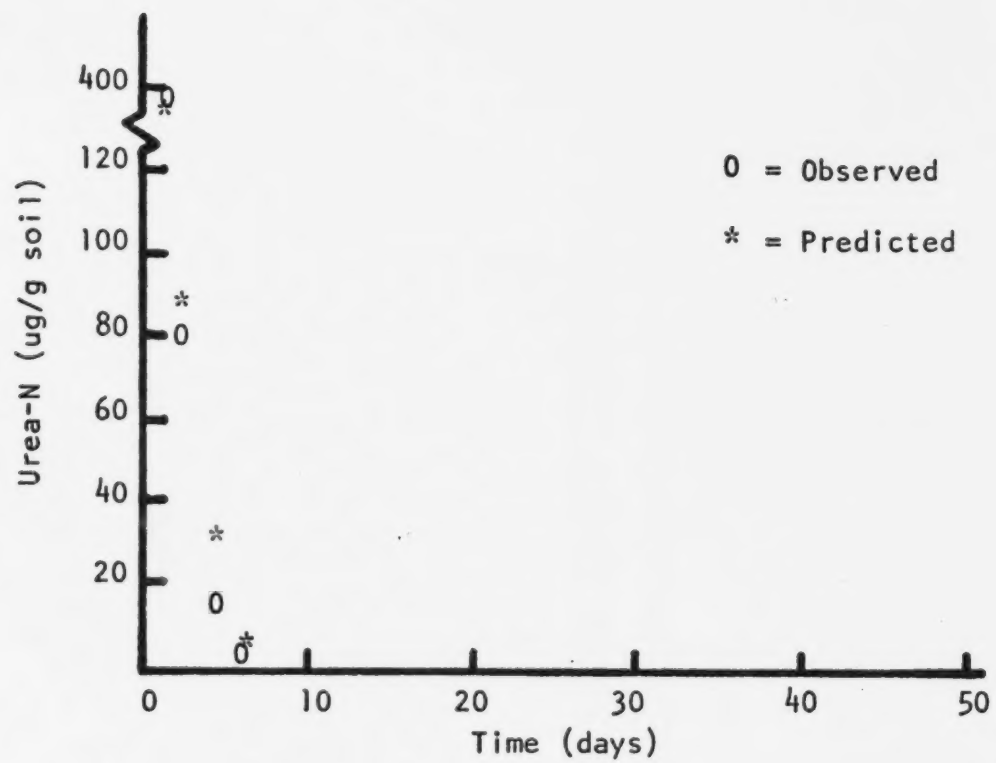


Fig. 4. Typical Observed and Predicted Curves for Urea-N

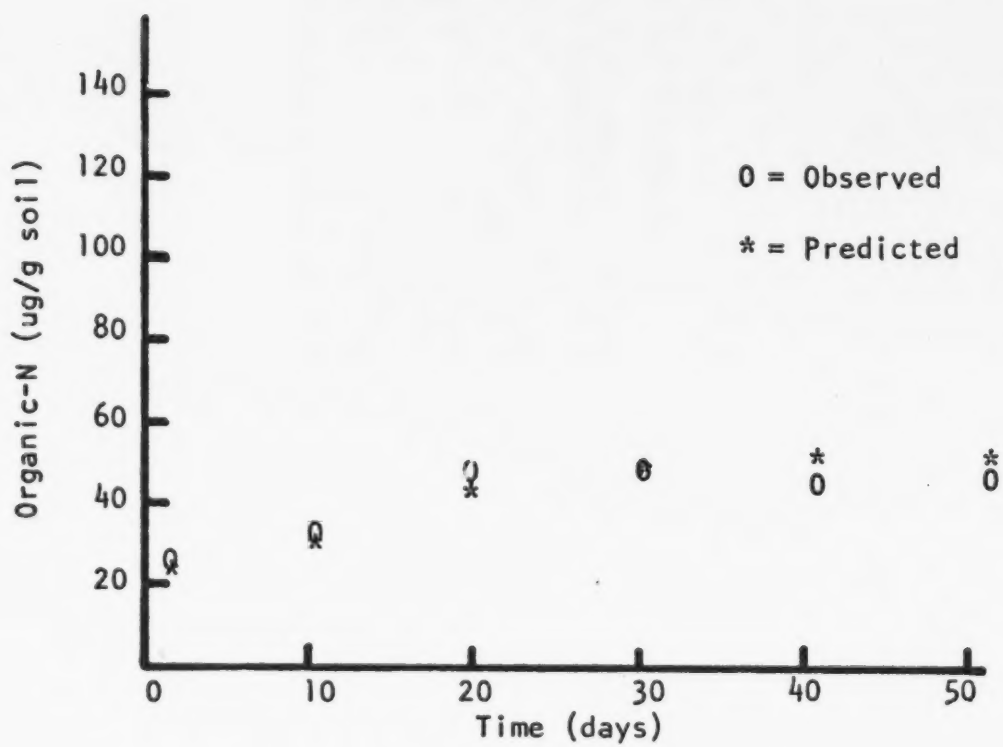


Fig. 5. Typical Observed and Predicted Curves For Organic-N

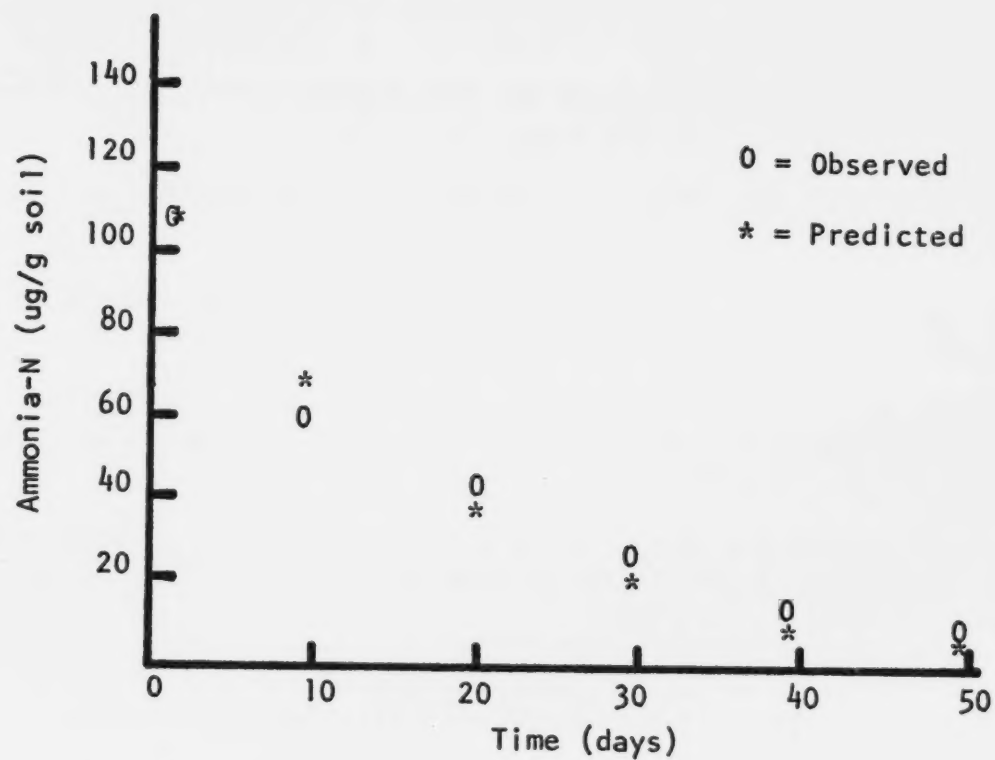


Fig. 6. Typical Observed and Predicted Curves for Ammonia-N

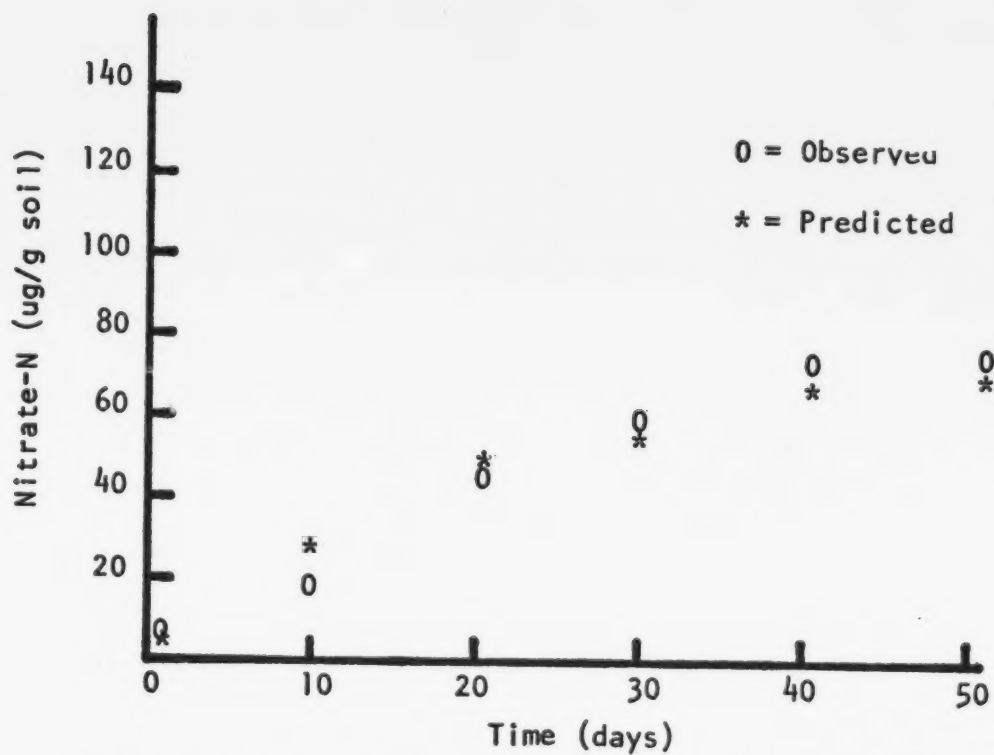


Fig. 7. Typical Observed and Predicted Curves for Nitrate-N

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THE MOVEMENT OF NITROGENOUS FERTILIZERS THROUGH SOIL COLUMNS

By

John W. Williford, Thomas C. Tucker,
Robert L. Westerman and Doyle R. Cardon¹

Introduction

Economic pressures have forced farmers to strive for maximum yields. As a result, gigantic amounts of fertilizers are being applied each year and the rates will probably increase each year. In the Continental United States over 6.5 million tons of N were applied last year. In the Pacific States (i.e., California, Oregon, and Washington) over 650,000 tons of N were applied.

With such large amounts of N being applied, we as Soil Scientists need to be concerned with the efficiency of applied fertilizer N. We need to determine the amount of fertilizer N taken up by the plant, the amount remaining in the soil after cropping and the amount that is lost by processes such as volatilization, denitrification and leaching.

In irrigated areas where excessive amounts of fertilizer N are being applied, nitrate pollution of ground waters could pose a serious problem. Therefore, we as Soil Scientists need to determine if nitrate pollution of ground waters is the result of inefficient fertilizer and management practices. This paper is a report of current work in progress from a cooperative project between the United States Bureau of Reclamation, Fresno, California, and the University of Arizona, Tucson. This work is a part of a broader investigation exploring the possibilities for the control of nitrogen in drainage water by modified practices at the source.

Methods and Material

Fourteen lysimeters made of techite (fibre glass) pipe 15 inches in diameter and 6.7 feet in length were filled with four major soil types from the west side of the San Joaquin Valley of California. Five columns were filled with Panoche fine sandy loam, a recent alluvial, light textured, slightly saline soil and three columns

¹ Research Soil Scientist, U.S. Bureau of Reclamation, Fresno, California; Professor, and Assistant Professor, respectively, Agricultural Chemistry and Soils, University of Arizona, Tucson; Natural Resources Specialist; U.S. Bureau of Reclamation, Fresno, California.

were filled with Panoche clay loam. Three columns were filled with Oxalis clay, a fine-textured soil, slightly to moderately compacted in the subsoil, and moderately saline. Three columns were filled with Lethent sandy clay loam, a basin-rim soil with a medium-textured surface over a moderately compacted fine-textured subsoil with moderate to strong concentrations of alkaline and saline salts. These soils were developed from sediments of the Coast Range Mountains. These lysimeters were located at Fresno at the Bureau of Reclamation field laboratory.

The soils were screened, weighed, placed in the columns and tamped to approximately field density.

The surface and subsurface soil material of the Panoche fine sandy loam, and the Oxalis clay soils were mixed when the lysimeters were filled. The soil material from the Panoche clay loam and the Lethent soils were placed in layered horizons in the same sequence as in the natural condition.

The lysimeters were instrumented with tensiometers, soil extract suction probes, and soil moisture and temperature cells. These instruments were placed in the soil columns by drilling holes through the sides of the lysimeters and inserting the instruments near the center of the soil columns. Generally four mercury-type tensiometers were located in each lysimeter at approximately 18-, 30-, 42- and 54-inch depths. Three each of the soil extract suction probes and the soil moisture and temperature cells were installed at approximately 12-, 36- and 60-inch depths. A typical layout of one lysimeter is shown in figure 1. When the lysimeters were filled, sufficient water was applied to the columns to bring the soils to field capacity and to start water draining from the lysimeters. After the columns started to drain, water was added in 4-inch increments every 2 weeks to leach the nitrates to a relatively constant level.

Soil extracts were collected from the suction probes at varying time periods, depending on the needs of the program, by applying approximately 35 pounds of suction with a vacuum pump. The lysimeters were designed to allow the leachate from the soil column to be collected at the bottom on the same schedule as the soil extracts.

The volumes extracted from the probes and collected in the leachates were recorded. All of the samples were analyzed for nitrates, electrical conductivity and pH. Some of the samples were analyzed for chlorides, ammonia, total nitrogen and atom percent excess ^{15}N .

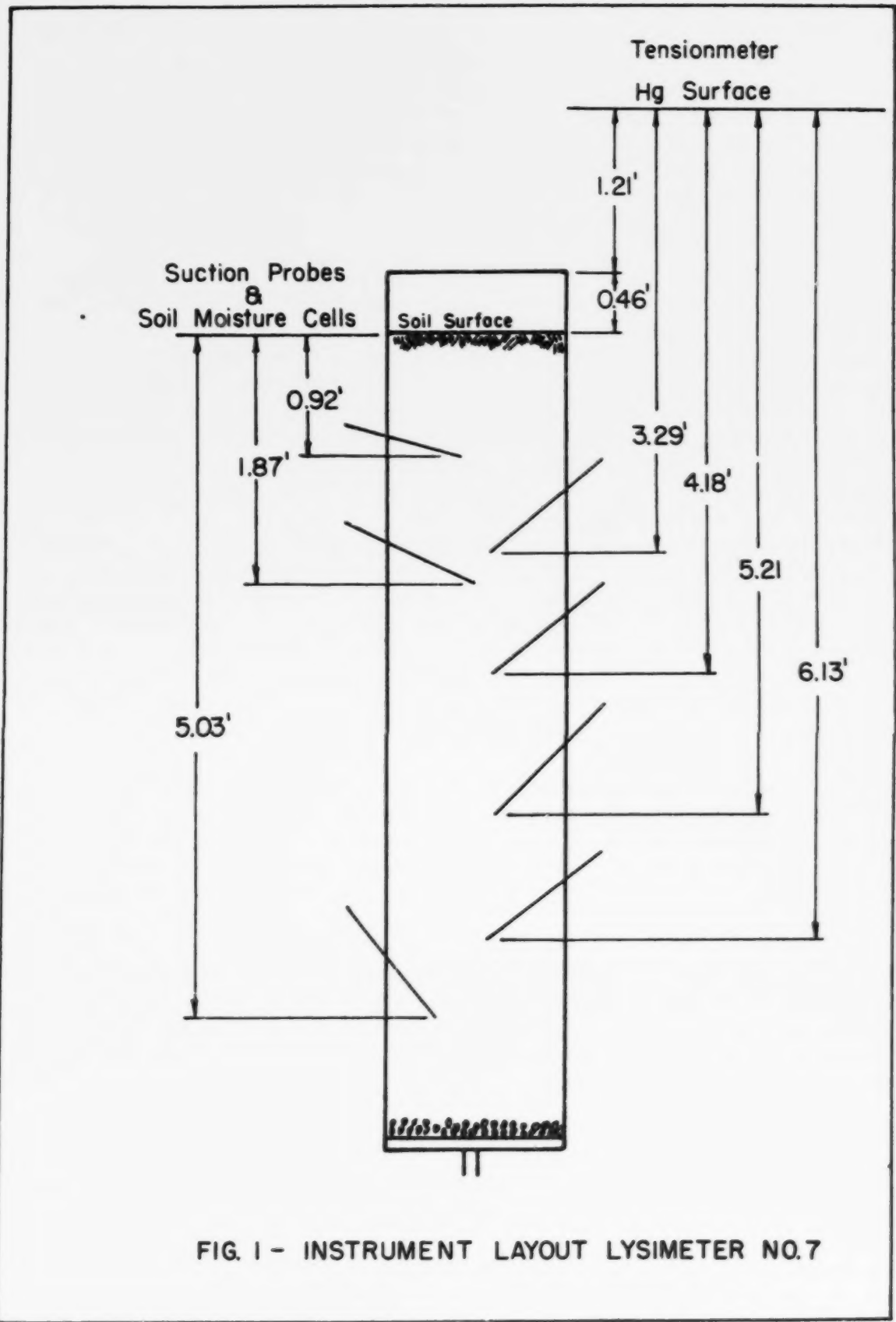


FIG. 1 - INSTRUMENT LAYOUT LYSIMETER NO. 7

The leaching program was continued until December 1968. At this time the nitrate concentrations in most of the lysimeters, although varying with soil type, were reduced to a fairly constant level. Barley was planted in the lysimeters and three different types of nitrogenous fertilizers were applied-- $(\text{NH}_4)_2\text{SO}_4$ and KNO_3 , fast nitrogen release types and sulfur-coated urea, a slow nitrogen release type. The fertilizers were applied at a rate equivalent to 100 pounds N per acre or 1,250 milligrams of N per lysimeter. The $(\text{NH}_4)_2\text{SO}_4$ and the KNO_3 fertilizers were enriched with approximately 10 percent ^{15}N and the urea with 28.2 percent ^{15}N . The $(\text{NH}_4)_2\text{SO}_4$ was applied to two lysimeters filled with Panoche clay loam and two filled with Oxalis clay. The KNO_3 was applied to two soil columns of Panoche fine sandy loam and two of Lethent sandy clay loam. Sulfur-coated urea was applied to two columns of Panoche fine sandy loam. A control to which no fertilizers were applied was maintained for each soil type. Samples from the suction probes and the leachates were collected, frozen and sent to the University of Arizona for analysis of nitrate and atom percent excess ^{15}N .

The barley was irrigated to approximately the rate that the farmers of the area use in their normal field operations. The soils were at field capacity when seeded and a total additional application of water of 9.2 inches was applied during the growing season. The irrigation water applied was obtained from a well at the University of California Westside Field Station near Five Points. This water contained approximately 2 milligrams per liter of NO_3 and 1,000 milligrams per liter of total dissolved solids.

After the barley was harvested in May the lysimeters were irrigated with 8 inches of water. This amount brought the soils to field capacity and sorghum was planted without additional fertilizers. Total water application was 25.4 inches in addition to the 8-inch preirrigation for the sorghum growing season. The sorghum was harvested in October 1969.

Grain from the barley and sorghum crops was weighed and analyzed separately from the straw or stover. All plant samples were dried, ground, and analyzed for total nitrogen by standard micro-Kjeldahl procedures. After titration, the ammonia was redistilled and atom percent excess ^{15}N determined.

Results and Discussion

The initial nitrate levels of the soils as determined from 1:1 water extracts ranged from 55 in the Panoche clay loam subsoil to 500 in the Lethent clay loam surface soil when the soils were brought from the field. The nitrate levels in leachates collected during initial

leaching and before fertilization ranged from 20,000 p.p.m. in the Oxalis clay to 2,500 p.p.m. in the Panoche fine sandy loam. These high levels are believed due primarily to the change in the environment of the soils as a result of the screening, mixing, and aeration with the resultant increased microbial activity, ammonification and nitrification of some of the native organic nitrogen. These high nitrate levels also indicate how relatively low levels of native nitrates can be concentrated in the ground water by leaching.

After the high initial nitrate concentration, a rapid drop in the nitrate levels occurred as additional water was moved through the columns. At this time the nitrate levels in the soil extracts from all sampling depths of the soil columns had been reduced to less than 10. The nitrates in the leachate of the several columns had been stabilized at values ranging from about 50 in the Panoche fine sandy loam to about 500 in the Oxalis clay. After the barley was planted and the ^{15}N enriched fertilizer applied, periodic samples were collected of the soil extracts at three depths in the columns and from the leachates. Data resulting from the analyses of these samples, based primarily on the atom percent excess ^{15}N , are presented in tables 1 through 7. These data are averages of values from duplicate columns of each treatment.

Data for nitrogen content and the percentage which is attributable to fertilizer -N in the "A" depths, 9 to 18 inches, are listed in table 1. These data show that at this depth the highest percentage of fertilizer -N appeared in those soils to which KNO_3 was applied. In Panoche fine sandy loam and Lethent sandy clay loam, respectively, 82 and 65 percent of the total nitrogen collected in the soil extract was fertilizer -N. By comparison, only 14 to 24 percent, respectively, of the N in the extract was fertilizer -N when $(\text{NH}_4)_2\text{SO}_4$ and sulfur-coated urea were the N sources.

This would indicate that much of the NH_4 -N is tied up by the clay complex of the soil near the soil surface. Since only 30 percent of the sulfur-coated urea was readily soluble and the remainder was treated to dissolve slowly, movement of nitrogen as urea could be expected to be approximately 30 percent of N movement from KNO_3 assuming appreciable hydrolysis did not occur. The data are in accord with these proportions. However, the system is complicated by N release from sulfur-coated urea, hydrolysis of urea, nitrification and soil textural differences; therefore, the apparent proportionality may have resulted from compensating effects.

Table 1 - Nitrogen Content and Percent of Fertilizer
Nitrogen in Soil Extracts from "A" Depths
December 16, 1968 - August 8, 1969

<u>Soil Type</u>	<u>Fertilizer</u>	<u>Depth</u>	<u>Total N</u>	<u>Fertilizer N</u>
		In.	mg	%
Panoche CL	$(\text{NH}_4)_2\text{SO}_4$	16	12.6	14.2
Panoche FSL	KNO_3	15	49.2	81.7
Lethent CL	KNO_3	9	34.1	65.0
Panoche FSL	S:Urea-N	11	15.2	23.7
Oxalis C	$(\text{NH}_4)_2\text{SO}_4$	18	16.2	14.07

The nitrogen content and the percent fertilizer nitrogen in the soil extract at the "B" depths, 24 to 39 inches, are listed in table 2.

Table 2 - Nitrogen Content and Percent of Fertilizer
Nitrogen in Soil Extracts from "B" Depths
December 16, 1968 - August 8, 1969

<u>Soil Type</u>	<u>Fertilizer</u>	<u>Depth</u>	<u>Total N</u>	<u>Fertilizer N</u>
		In.	mg	%
Panoche CL	$(\text{NH}_4)_2\text{SO}_4$	39	22.6	2.1
Panoche FSL	KNO_3	39	22.3	4.5
Lethent CL	KNO_3	24	14.1	22.3
Panoche FSL	S:Urea-N	33	14.2	3.4
Oxalis C	$(\text{NH}_4)_2\text{SO}_4$	31	36.0	0.7

The percent of fertilizer -N of the total N collected in the B depth was less than 4.5 with the exception of the Lethent clay loam. The relatively high percentage of fertilizer N in the Lethent columns was probably caused by the higher position of the suction probes in the columns. These low values for the other columns indicate that little movement of any of the fertilizers occurred to depths of 31 to 39 inches.

The nitrogen content and percent fertilizer N for the "C" depth are listed in table 3. At the most 4 percent of the N collected from the probe came from the applied fertilizer. The highest percentage of fertilizer N was from the Lethent soil and least smallest was from the Oxalis. These low values again indicate that a very small percentage of the applied N moved through the soil columns.

Table 3 - Nitrogen Content and Percent of Fertilizer
Nitrogen in Soil Extracts from "C" Depths
December 16, 1968 - August 8, 1969

Soil Type	Fertilizer	Depth	Total N	Fertilizer N
		In.	mg	%
Panoche CL	$(\text{NH}_4)_2\text{SO}_4$	63	25.1	1.6
Panoche FSL	KNO_3	62	39.3	2.1
Lethent CL	KNO_3	60	19.7	4.2
Panoche FSL	S:Urea-N	58	19.0	1.2
Oxalis C	$(\text{NH}_4)_2\text{SO}_4$	56	20.0	0.9

The total nitrogen removed in the leachate and the percent of this total that was fertilizer -N are listed in table 4. The total N removed from the soil columns ranged from 156 to 442 milligrams; however, of these amounts only 0.7 percent or less was from fertilizer N.

Table 4 - Nitrogen Content and Percent Fertilizer N in the
Leachate - December 16, 1968 - August 1, 1969

Soil Type	Fertilizer	Total N	Fertilizer N
		mg	%
Panoche CL	$(\text{NH}_4)_2\text{SO}_4$	206	0.5
Panoche FSL	KNO_3	404	0.6
Lethent CL	KNO_3	156	0.7
Panoche FSL	S:Urea-N	273	0.4
Oxalis C	$(\text{NH}_4)_2\text{SO}_4$	442	0.1

The total nitrogen removed from all soil extracts and leachates and the percentage of these values that were fertilizer -N are listed in table 5. Although the total N ranged from 224 milligrams in the Lethent clay loam to 515 milligrams in the Panoche fine sandy loam only a small percentage of these totals were from fertilizer -N. The percentages of fertilizer N recovered varied from 0.6 percent in the Oxalis clay to 12.5 percent in the Lethent clay loam. The higher percentages of fertilizer -N recovered from those columns using KNO_3 are due primarily to the large quantities extracted from the "A" and "B" depths in these soils.

Table 5 - Total Nitrogen Content of Soil Extracts,
Leachates and Percent Fertilizer N
December 13, 1968 - August 1, 1969

Soil Type	Fertilizer	Total N (Soil + Fertilizer)	Fertilizer N
		mg	% of Total N
Panoche CL	(NH ₄) ₂ SO ₄	266	1.3
Panoche FSL	KNO ₃	515	8.7
Lethent CL	KNO ₃	224	12.5
Panoche FSL	S:Urea-N	321	1.7
Oxalis C	(NH ₄) ₂ SO ₄	515	0.6

The fertilizer -N recovered as a percentage of the total fertilizer applied is listed in table 6. The largest percentage, 3.58 of the fertilizer -N recovered was from the Panoche fine sandy loam soil treated with KNO₃ fertilizer. The smallest percentage, 0.26 or 3.3 milligrams, was from the Oxalis clay which was treated with (NH₄)₂SO₄. The most significant of these data are the amounts of N recovered in the leachates. This is the quantity which under field conditions would go into the ground water. The data show that the largest percentage of fertilizer -N was recovered from the leachate of the light-textured soil treated with KNO₃. It was a very small amount, representing 0.23 percent or 2.9 milligrams, of the total fertilizer applied. The least amount, 0.04 percent or 0.5 milligrams was recovered from the heavy Oxalis clay soil that was treated with (NH₄)₂SO₄.

Table 6 - Recovery of Fertilizer N from all
Probes and Leachates
December 13, 1968 - August 1, 1969

Fertilizer	Soil Type	Sample Depth									
		A		B		C		L		Total	
		%	mg	%	mg	%	mg	%	mg	%	mg
(NH ₄) ₂ SO ₄	Pan.CL	.14	1.8	0.04	.5	0.03	.4	0.07	.9	.28	3.6
KNO ₃	Pan.FSL	3.21	40.1	0.08	1.0	0.07	.9	0.23	2.9	3.58	44.8
KNO ₃	Let.CL	1.81	22.6	0.27	3.4	0.07	.9	0.09	1.1	2.24	28.0
S:Urea-	Pan.FSL	0.30	3.8	0.04	.5	0.02	.3	0.09	1.1	.45	5.7
(NH ₄) ₂ SO ₄	Ox. C	0.19	2.4	0.02	.3	0.01	.1	0.04	.5	.26	3.3

The amounts of nitrate -N in leachates from various soil columns treated with fertilizers and similar columns in which no fertilizers were applied are listed in table 7.

The amount of $\text{NO}_3\text{-N}$ removed varied in the fertilized columns from 910 milligrams in the Oxalis clay to 145 milligrams in the Panoche clay loam and in the control columns from 788 milligrams in the Oxalis clay to 133 milligrams in the Panoche clay loam. As noted in table 6 the maximum amount of fertilizer -N recovered in the leachate was 0.23 percent or 2.9 milligrams in the Panoche fine sandy loam soil treated with KNO_3 . Lesser amounts of fertilizer -N were recovered from the other columns. Although apparent differences existed between the controls and the fertilized columns (table 7) these differences probably were due to analytical and soil variability rather than contributions from the applied fertilizers.

The significance of these data showing relatively large amounts of nitrogen removed from the columns is that only a very small percentage come from the applied fertilizers. Since the N in the leachate did not originate from the fertilizer and the amount in the applied water was small, it had to come from the native nitrogen in the soil.

Table 7 - Nitrate -N Recovered in the
Leachate of Soil Columns
December 16, 1968 - August 18, 1969

Soil Type	Fertilizer	Nitrate-N in Leachate	
		Control	Fertilized
		mg	
Panoche CL	$(\text{NH}_4)_2\text{SO}_4$	133	145
Panoche FSL	KNO_3	281	386
Lethent CL	KNO_3	443	286
Panoche FSL	S:Urea-N	281	209
Oxalis C	$(\text{NH}_4)_2\text{SO}_4$	788	910

The percentages of applied fertilizer -N recovered by cropping are listed in table 8. The highest percentage recovery by the barley was 73 percent from the Panoche fine sandy loam treated with KNO_3 . The lowest recovery, 47 percent, was from Panoche fine sandy loam which was assumed to be due to the slow N release rate of the sulfur-coated urea. The recovery rates in the other treatments ranged from 63 to 66 percent.

The percentage of recovery by grain sorghum of the applied fertilizer -N was greatest, 13.5 percent, in the Panoche fine sandy loam treated with the sulfur-coated urea. The large recovery rate in this treatment was due to the greater amount of residual N remaining

in the soil as a result of the slow release of N from sulfur-coated urea. The recovery rates in the other treatments ranged from 2.3 to 3.7 percent.

Table 8 - Recovery of Applied Fertilizer Nitrogen
in the Barley May 1969 and
Grain Sorghum October 1969

Fertilizer	Soil Type	Barley (% AFN)			Grain Sorghum (% AFN)		
		: Straw	Grain	Total	: Straw	Seed	Total
(NH ₄) ₂ SO ₄	Panoche CL	17.9	47.7	65.6	1.00	1.87	2.87
KNO ₃	Panoche FSL	18.8	54.3	73.1	.78	2.89	3.67
KNO ₃	Lethent CL	17.4	47.9	65.3	.76	1.51	2.28
Urea-S	Panoche FSL	8.9	38.4	47.3	3.75	9.78	13.53
(NH ₄) ₂ SO ₄	Oxalis C	24.5	38.2	62.7	1.60	1.45	3.05

The percentages of the applied fertilizer -N recovered by barley, grain sorghum and in the water samples collected between December 16, 1968 and August 8, 1969, are listed in table 9. They ranged from a maximum 80.3 percent in Panoche fine sandy loam treated with KNO₃ to a minimum of 61.3 percent in Panoche fine sandy loam treated with sulfur-coated urea. The recovery from the other systems ranged from 65.9 to 69.8 percent. The high percentage recovery from Panoche fine sandy loam soil treated with KNO₃ was assumed to be due to the NO₃-N form of fertilizer being more readily available in the lighter-textured soil because of increased mobility in the root-sorbing zone.

These data show that a minimum of 19.7 and a maximum of 38.7 percent of the applied fertilizer -N in the various soil columns was unaccounted for. The unaccounted-for portions are speculated to have been the result of one or more of the following: (a) lost by volatilization and denitrification, (b) tied up in the plant roots, (c) adsorbed on the clay complex, (d) converted to an organic N form by soil bacteria, and (e) remained in solution in the soil columns.

A portion of the residual N could be leached from the columns at a later date. To check this, water is still being applied to the columns and the leachate collected; however, at this date no additional data are available.

Table 9 - Recovery of Applied Fertilizer N in
Barley, Grain Sorghum, and Water Samples
Harvested December 1968 - October 1969

<u>Fertilizer</u>	<u>Soil Type</u>	<u>Barley</u> %	<u>Grain Sorghum</u> %	<u>Water Samples</u> %	<u>Total</u> %
(NH ₄) ₂ SO ₄	Panoche CL	65.6	2.87	0.28	68.75
KNO ₃	Panoche FSL	73.0	3.67	3.59	80.26
KNO ₃	Lethent CL	65.3	2.28	2.24	69.82
S:Urea-N	Panoche FSL	47.3	13.53	0.45	61.28
(NH ₄) ₂ SO ₄	Oxalis C	62.1	3.05	0.26	66.01

Summary

Relatively large quantities of N were removed in the leachates; however, less than 0.23 percent of this came from fertilizer -N.

Although all the quantities were small, the maximum fertilizer -N recovered in the leachate was from the lighter-textured Panoche fine sandy loam soil treated with KNO₃. The minimum recovered was from the heavy-textured Oxalis clay treated with (NH₄)₂SO₄.

A larger fraction of the fertilizer -N was found at the lower depths on the light-textured soils and on those soils treated with KNO₃. In the fine-textured soils little movement of the fertilizer N was observed below the 30-inch depth.

During the period of this study, December 16, 1968, to approximately October 1969, a maximum of 80.3 percent and a minimum of 61.3 percent of the applied fertilizer -N was recovered from the soil columns by the crops, soil extracts and leachates. The maximum amount was recovered from Panoche fine sandy loam soil treated with KNO₃ and the minimum was recovered from the Panoche fine sandy loam treated with the slow-release sulfur-coated urea.

Differences in the percentage of fertilizer -N recovered in the leachate were small and apparently related to the type of ion in which the nitrogen occurs rather than to fast or slow release fertilizer.

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AGRICULTURAL NITRATE REDUCTION AT A WATER TABLE¹

By

L. S. Willardson and Burl D. Meek²

Introduction

The agricultural industry in the United States is responsible for the application of 6 million tons of nitrogen fertilizer to the soil every year. Fertilizer trials on research stations have indicated that approximately 50 percent of the applied nitrogen can be accounted for in the crop grown. The conclusion could be drawn from this information that 3 million tons of nitrogen enters the ground-water system of the United States annually from agricultural sources. In 1966, however, 9 million tons³ of nitrogen were removed from the soil by agricultural crops. This does not include nitrogen removed from pasture and rangeland. With 6 million tons applied and 9 million tons removed, agriculture would seem to be responsible for annually mining 3 million tons of soil nitrogen. The true disposition of nitrates applied as fertilizers is largely unknown at the present time.

An experiment on the chemistry of ground water on an irrigated farm in the Imperial Valley⁴ showed that ground water contains varying amounts of nitrate depending on the depth of sampling. Nitrate appeared in the soil solution above the water table but was virtually absent below the water table. A laboratory study carried out by Meek⁴ indicated that denitrification was taking place in the soil solution near the water table.

Meek showed that by creating saturated soil conditions in the presence of bacteria and a source of energy such as organic carbon, anaerobic conditions would develop in which reduction of nitrate would take place. The bacteria decomposed the nitrate molecule to obtain oxygen, liberating the nitrogen as nitrogen gas. This process commonly occurs in saturated or nearly saturated soils.

¹ Contribution of the Agricultural Research Service, Soil & Water Conservation Research Division, Southwestern Irrigation Field Station, Brawley, California.

² Research Investigations Leader and Soil Chemist, Southwestern Irrigation Field Station, P. O. Box 1339, Brawley, California.

³ White, W. C. Plant Nutrient Toll. 1965 Harvest. USA Plant Food Review, p. 16, Winter 1965.

⁴ Meek, B. D., L. B. Grass, and A. J. MacKenzie, Applied Nitrogen Losses in Relation to Oxygen Status of Soil. Soil Sci. Soc. Proc. Vol. 33, No. 4, July-August 1969.

Research at the Southwestern Irrigation Field Station has indicated this denitrification process can be managed in field soils to prevent movement of agricultural nitrate into the ground water.

Soil Column Experiment

A special laboratory was constructed at the Southwestern Irrigation Field Station to study the chemistry of water moving through a soil profile toward a water table and then below the water table into submerged drains. Six soil columns 15 inches in diameter and 10 feet deep were constructed such that drains could be placed at 6-, 8- and 10-foot depths with the controlled water table at 6 feet. The columns were filled with a local soil profile in a disturbed state but in the natural order. The soil columns were instrumented with soil solution samplers, platinum electrodes for measuring redox potential, porous cups for soil atmosphere samples, and tensiometers for inferring soil moisture content. The effluent from the drains was collected for analysis. Nitrate fertilizer at a rate of 100 pounds of nitrogen per acre was applied in the first irrigation water. Four irrigations were required to move the nitrate concentration peak from the surface to the 6-foot water table. Denitrification took place below the water table and in the nearly saturated soil immediately above the water table.

Field Experiment

On the basis of results obtained on the Drainage Research Farm and from the soil column study, an experiment was installed in the field to test the concept of controlled denitrification by means of submerged drains. The experiment is located on the farm of John Nakamura near Firebaugh, California, on the west side of the San Joaquin Valley. The soil profile is a Panoche silt loam surface soil, a sandy loam horizon at 7.5 feet and a clay layer at approximately 9 feet. The clay layer appears a few miles to the north as a surface soil. The Bureau of Reclamation and Soil Conservation Service are cooperators with the Agricultural Research Service on the project.

The experimental drainage system consists of a main collector line 8 inches in diameter and 1,850 feet long with 6 lateral lines 6 inches in diameter having a total length of 4,900 feet. The drains were installed with a trenching machine. Washed concrete sand envelope material was placed around the drains at a rate of 18 tons per 100 lineal feet. Concrete pipe with tongue and groove joints in 2-foot lengths was used throughout. The drains were installed 6, 7.5 and 9 feet deep. The main collector line was installed at a depth of 11 feet at the drainage sump. A standpipe was installed in the sump to control the field water table at the

6-foot depth. This provided 0, 1.5, and 3 feet of submergence for two drains at each depth. Water sampling tubes were installed in the lateral lines at the time of installation. Sampling tubes were placed inside the laterals near the outlet of each drain. Approximately 200 feet from both ends of the lateral lines, solution samplers were installed in modified pipe sections to extract water samples from eight positions around the exterior surface of the drain. The purpose of these samplers was to obtain water that had moved along various flow paths through the soil. Additional soil solution samplers were installed in the soil at 4.5-, 6-, 7.5- and 9-foot depths at the tile line and at the one-third points between drains. The 4.5-foot depth sampler was equipped with a porous cup for obtaining water samples in the unsaturated zone above the water table. A layout of the field is shown in figure 1.

Following installation of the drains, the field was irrigated to consolidate the backfill in the trenches. After a smoothing operation, sorghum was planted. The crop was irrigated four times during July and August of 1969. Water samples were collected from the sampling system prior to and periodically following each irrigation. The water samples were analyzed for electrical conductivity, dissolved oxygen, nitrate-nitrogen, organic carbon and pH. Iron and manganese were present in very small amounts.

Results

The data from the soil column experiment are shown in figure 2. The curves show the nitrate-nitrogen concentration in the profile following successive irrigations. The peak nitrate-nitrogen concentration in the soil solution after application of an equivalent of 100 pounds of nitrogen per acre as ammonium nitrate was 50 p.p.m. As subsequent irrigations moved the concentration peak lower in the profile, the nitrate-nitrogen content diminished. Safflower plants were growing on the columns at the time. As the concentration peak approached the water table and entered the capillary fringe, denitrification occurred. Approximately 50 percent of the nitrate present at the 5-foot depth was reduced in the zone from 5 to 6 feet.

In the columns where the drains were submerged 2 and 4 feet, the drain effluent had only 0.5 p.p.m. nitrate-nitrogen. There was still some organic carbon in solution, indicating that additional nitrate could have been removed.

Data from the soil solution samplers showed nitrate-nitrogen levels in solution between the drains as high as 1,000 p.p.m. (figure 3). The very high nitrogen contents were measured at the 7.5-foot depth and were only slightly affected by irrigation. Nitrate-nitrogen contents at the shallower depths were lower and were decreased by irrigation.

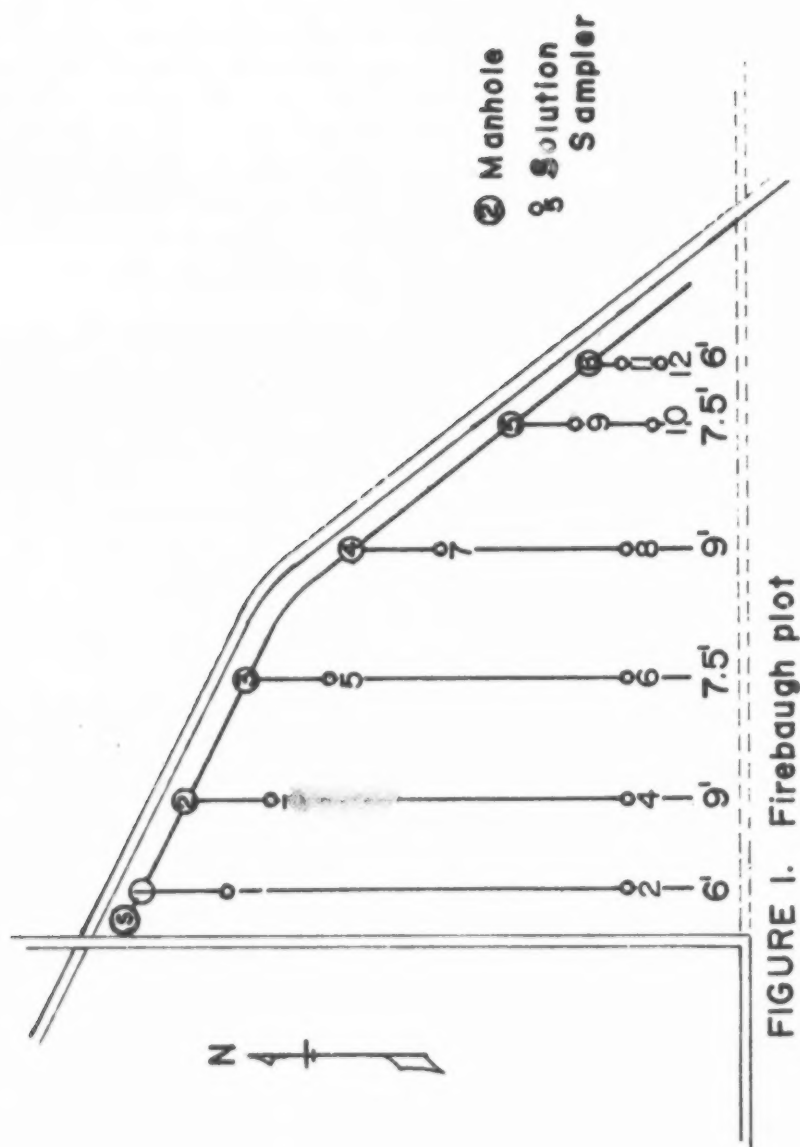


FIGURE 1. Firebaugh plot

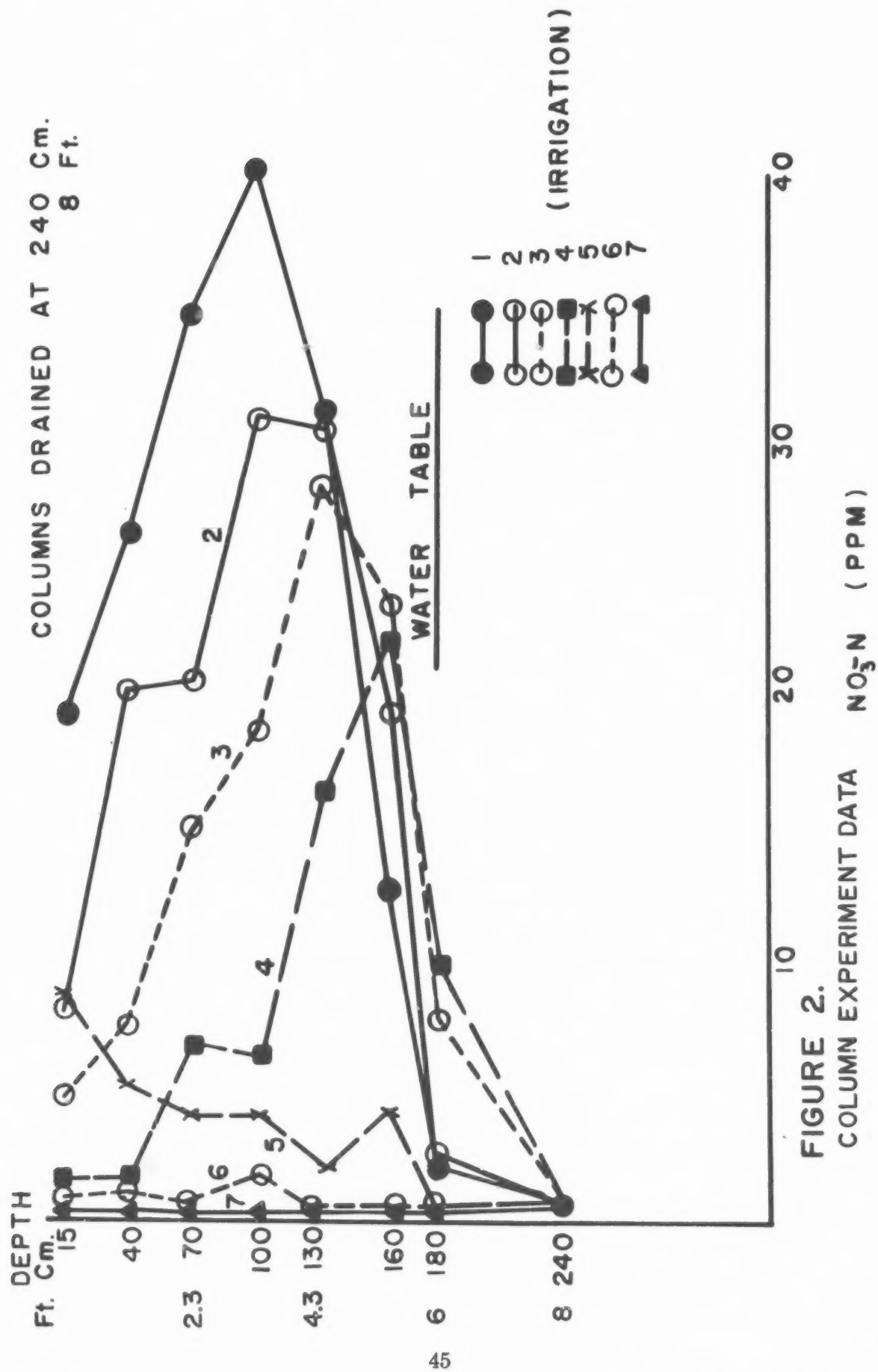


FIGURE 2.
COLUMN EXPERIMENT DATA NO₃-N (PPM)

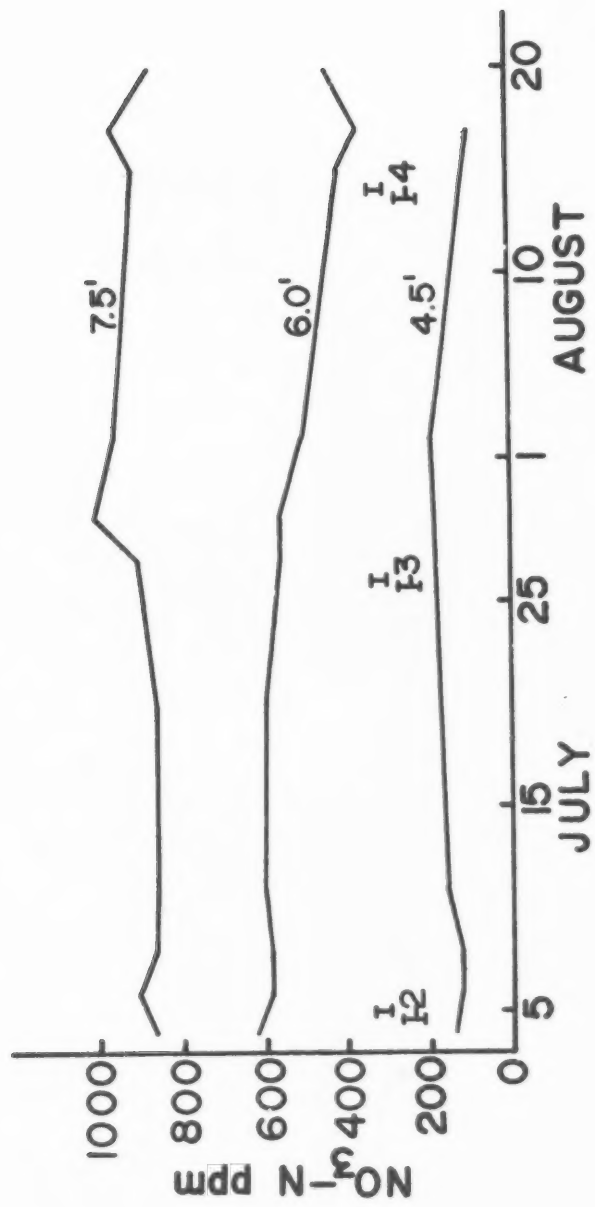


FIGURE 3. $\text{NO}_3\text{-N}$ between drains

Figure 4 shows some of the nitrate data collected around three of the drains before and after the third irrigation. The water table was slightly above the 6-foot depth, allowing collection of a saturation sample. Low nitrate concentrations occurred at the tops of the 6-foot and 9-foot drains and varied following irrigation. Nitrate-nitrogen contents of the water around the 7.5-foot drain remained relatively high. Water samples were taken inside the drains at the same locations.

Electrical conductivities were measured on all water samples. High conductivities were generally related to high nitrate contents but there was not a strong correlation. Figure 5 shows the electrical conductivities of the samples corresponding to the nitrate data shown in figure 4. Conductivities decreased at the 6- and 7.5-foot depths following irrigation but increased with time at the 9-foot depth.

Organic carbon data are not shown but varied between 20 and 50 p.p.m. in the plot.

Discussion

The soil column experiment showed that denitrification can be effected by establishing a water table above the drains, providing a saturated flow path in which anaerobic conditions can develop. The soil in the columns came from a cultivated field and the amount of organic carbon in the soil solution from crop residues and decaying roots was sufficient for denitrification. The soil in the columns was relatively fine textured, resulting in a low percolation rate. The crop growing in the columns undoubtedly extracted part of the nitrate-nitrogen as the solution moved through the profile. Important denitrification occurred in the capillary fringe above the 6-foot depth even where the drain was not submerged. Where proper conditions can be established, i.e., an oxygen shortage, adequate organic carbon as an energy source, and a bacterial population, anaerobic conditions will develop which will result in denitrification.

The field experiment at Firebaugh illustrates the effect that a lack of one of the denitrification components mentioned above can have. The water collected in the samplers at the 7.5-foot depth had a high nitrate content and 20 to 50 p.p.m. organic carbon. The fact that the organic carbon was not taken down to a low level indicates that suitable bacteria were not present or that the carbon was in a form that could not be used. The general level of dissolved oxygen in the same water was 1 to 2 p.p.m., which is higher than the 1-p.p.m. level present in the submerged zone of the laboratory columns. The normal level of dissolved oxygen in water from tile drains is 4 to 6 p.p.m. If suitable bacteria were present, dissolved oxygen and organic carbon would be lower.

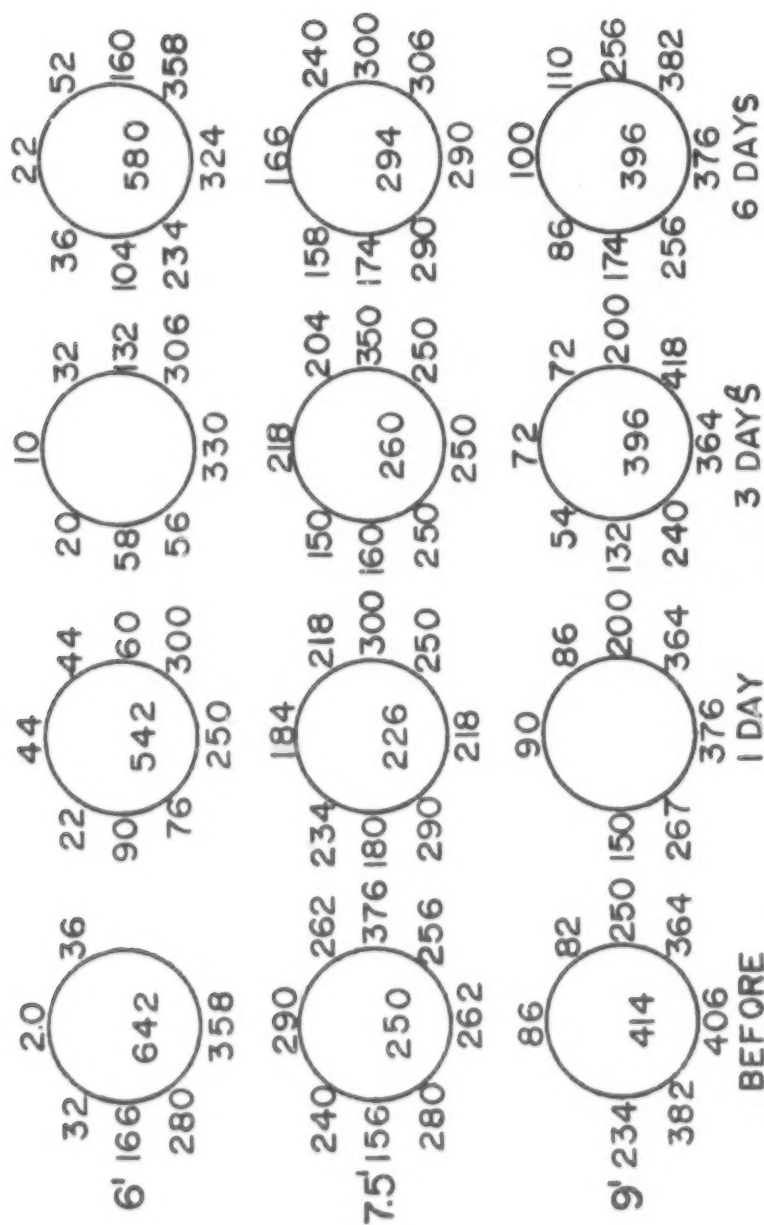


FIGURE 4. $\text{NO}_3\text{-N}$ ppm Irrigation 3

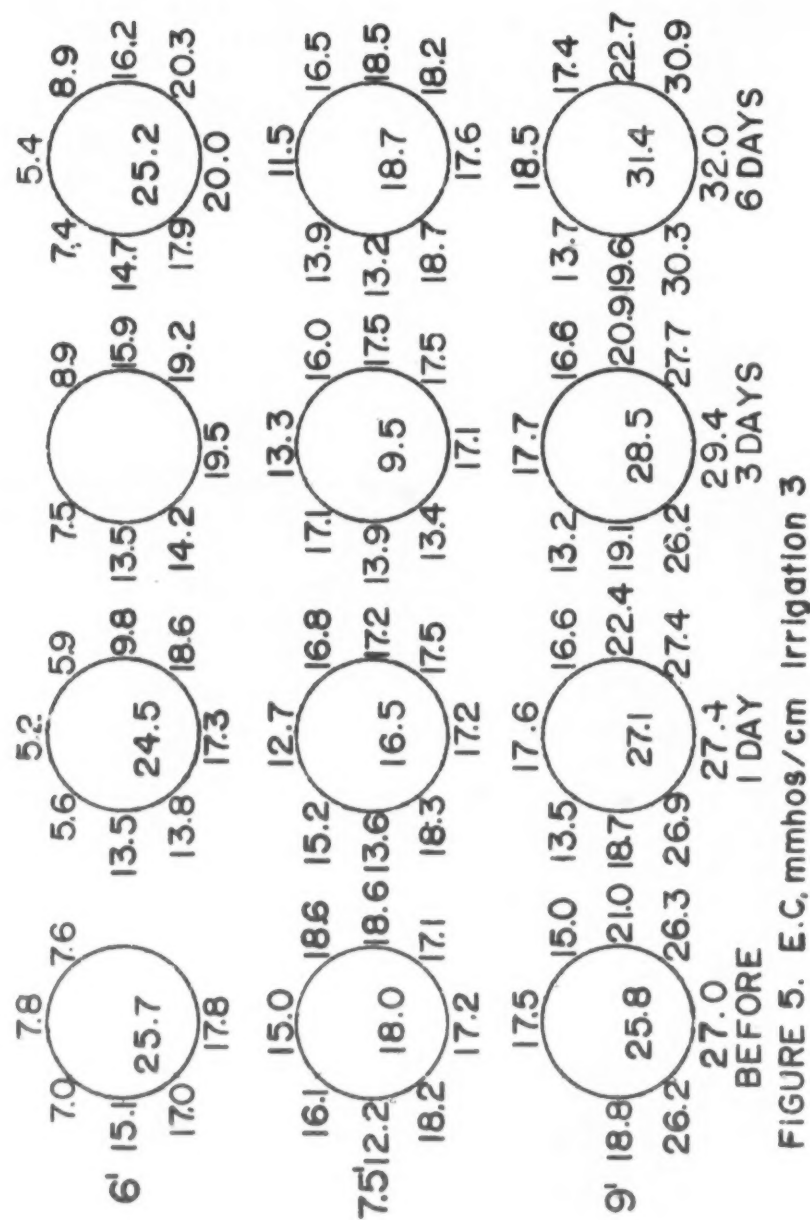


FIGURE 5. E.C. mmhos/cm Irrigation 3

Based on the results obtained in the columns, a nitrate-nitrogen content of 500 p.p.m. in the ground water would require a surface application of 1,000 pounds per acre of nitrogen as a nitrate fertilizer in a single application. The farmer customarily applies 100 pounds of nitrogen as NH_3 during the season. The gross difference in magnitude of nitrate contents indicates that the native ground waters are bringing nitrate to the area. The soils map for the area shows a band of relatively light-textured soil running upslope from the experiment location. The upslope area is arid to semiarid and is a likely contributing source of natural nitrate to the ground water. The contribution of agriculturally applied nitrate appears to be minimal.

The high nitrate content of the ground water suggests the possibility of dilution and use of the water as fertilizer. The electrical conductivity is too high, however, and use of even the diluted water as a fertilizer would result in salination of the soil.

The intensive sampling program at the Firebaugh location has emphasized the variability that can occur in such a field experiment. The nonuniformity of ground-water quality flowing into the drainage system is illustrated in figure 4. At the 6-foot depth on the day before irrigation the highest measured nitrate-nitrogen content outside the drain was 358 p.p.m. Ground water upstream from the sampling point obviously has a much higher nitrate content. Samples taken along the drains generally indicated a decrease in nitrate content as the main collector line was approached. The drain at the 9-foot depth before irrigation showed a nitrate-nitrogen content of 414 p.p.m. At another sampling point downstream in the same drain, the nitrate content decreased to 226 p.p.m. Denitrification inside the drain is limited, so mixing with other waters in the system is indicated. In some drains, the nitrate and conductivity change in the same direction; in other drains, they change in opposite directions.

The net result of the installation of the submerged drainage system has been to decrease the nitrate-nitrogen content of the drainage water. Figure 6 shows that for the final irrigation of the season, conductivity of the drain effluent from the total plot remained constant and the nitrate-nitrogen content decreased. If dilution alone were responsible for the decreased nitrate level, the electrical conductivity would also be lower.

It is doubtful that the submerged drains in the experiment will be able to denitrify the native ground waters entering the system. By dilution with the denitrified water from the irrigation, however, the nitrate content of the drainage water will be reduced.

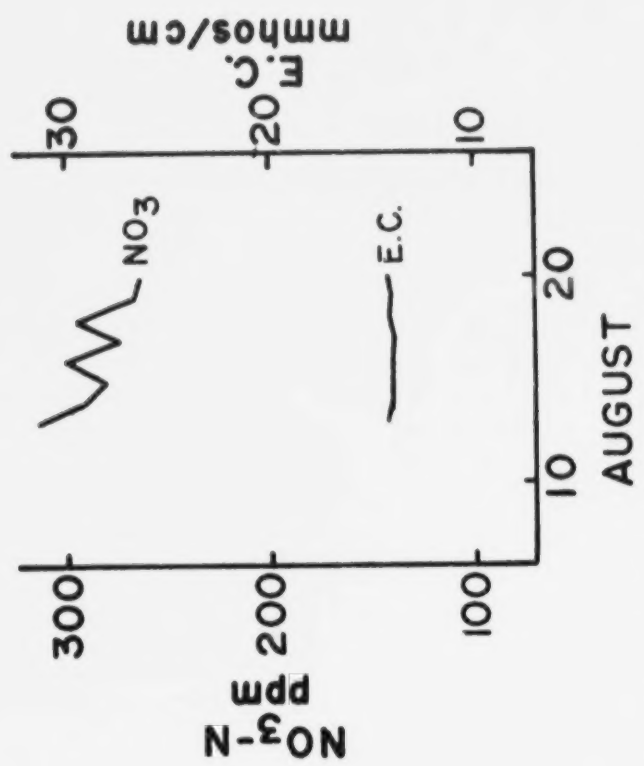


FIGURE 6. NO₃-N and E.C. for total plot
4th irrigation

Summary

Laboratory studies on large soil columns with a controlled water table and submerged drains have shown that very low nitrate content water can be delivered from agricultural drains. A field experiment on drain submergence which intercepts ground water high in native nitrate indicates that denitrified water from irrigated agriculture can reduce nitrate concentrations in drainage water by dilution.

MONITORING NUTRIENTS AND PESTICIDES IN SUBSURFACE AGRICULTURAL DRAINAGE

By

L. R. Glandon, Jr., and L. A. Beck¹

Introduction

The central valley of California is composed of two large valleys: the Sacramento in the north and the larger San Joaquin Valley in the south. The latter is approximately 300 miles long and 40 miles wide and is characterized by several streams from the Sierra Nevada and intermittent creeks from the Coastal Range. The San Joaquin Valley is divided into two drainage basins: the San Joaquin Drainage Basin which drains northward and empties into the eastern end of San Francisco Bay, and the Tulare Lake Basin where waters are impounded during years of excessive runoff.

San Joaquin Valley Drainage Investigation

The San Joaquin Valley Drainage Investigation was started in 1957.⁽¹⁾² The objectives were: (a) to define existing potential drainage problem areas, (b) to define the quantity and quality of drainage waters produced within these problem areas, and (c) to develop a plan for disposing of these drainage waters without creating problems in any of the surface or subsurface waters of the San Joaquin Valley or the receiving waters to which the drainage waters would be disposed. The quality portion of the investigation was expanded in 1963 by initiating two pesticide monitoring programs; intensified nutrient sampling started in 1966.

The purpose of this paper is to present data regarding the concentrations of nitrogen, phosphorus, and chlorinated hydrocarbon pesticides observed in agricultural subsurface drainage from tiled areas of the San Joaquin Valley in California.

¹ Water Resources Technician; Chief, Quality and Treatment Unit, California Department of Water Resources, Fresno, California, respectively.

² Parenthetical numbers refer to literature cited.

Objectives of Nutrient and Pesticide Investigations

The objectives of the nutrient and pesticide monitoring programs were as follows:

- a. To determine average concentrations and seasonal variations of nitrogen, phosphorus, and chlorinated hydrocarbon pesticides in existing tile drainage in the San Joaquin Valley.
- b. To determine the effects of agricultural practices such as irrigation, fertilization, and cropping patterns upon nutrient concentrations in tile drainage.
- c. To define areas having high concentrations of nutrients in the tile drainage effluent.
- d. To determine possible existing relationships between nutrient concentrations observed in tile drainage and physiographic positions and soil series.
- e. To evaluate pesticide use and production data in relation to pesticide concentrations observed in tile drainage.

Area of Investigation and Methods

The San Joaquin Valley was divided into three general areas of study where numerous tile drainage systems have been installed. A map of the drainage problem areas and their locations is presented in figure 1. The number of tile drainage systems in each of the three areas, their physiographic positions (2), and the soil series is given in table 1.

Northern Area. The northern area extends from Byron to Gustine. The tile drainage systems in this area occupy three physiographic positions. Most of the tile drainage systems have been installed in areas of the Sorrento soil series. Prior to 1940, much of the farming in this area was devoted to hay, grain, and pasture with little fertilization.

Central Area. The central area extends from Gustine to Mendota; tile drainage systems in this area also occupy three physiographic positions. The Panoche soil is the dominant series in the area studied. Cropping within the central area is very diversified and includes cotton, alfalfa, melons, rice, and vegetable crops. Fertilizers have been used freely for the past 25 or more years.

Southern Area. The southern area is essentially within the confines of the Tulare Lake Basin. Tile drainage systems in the southern

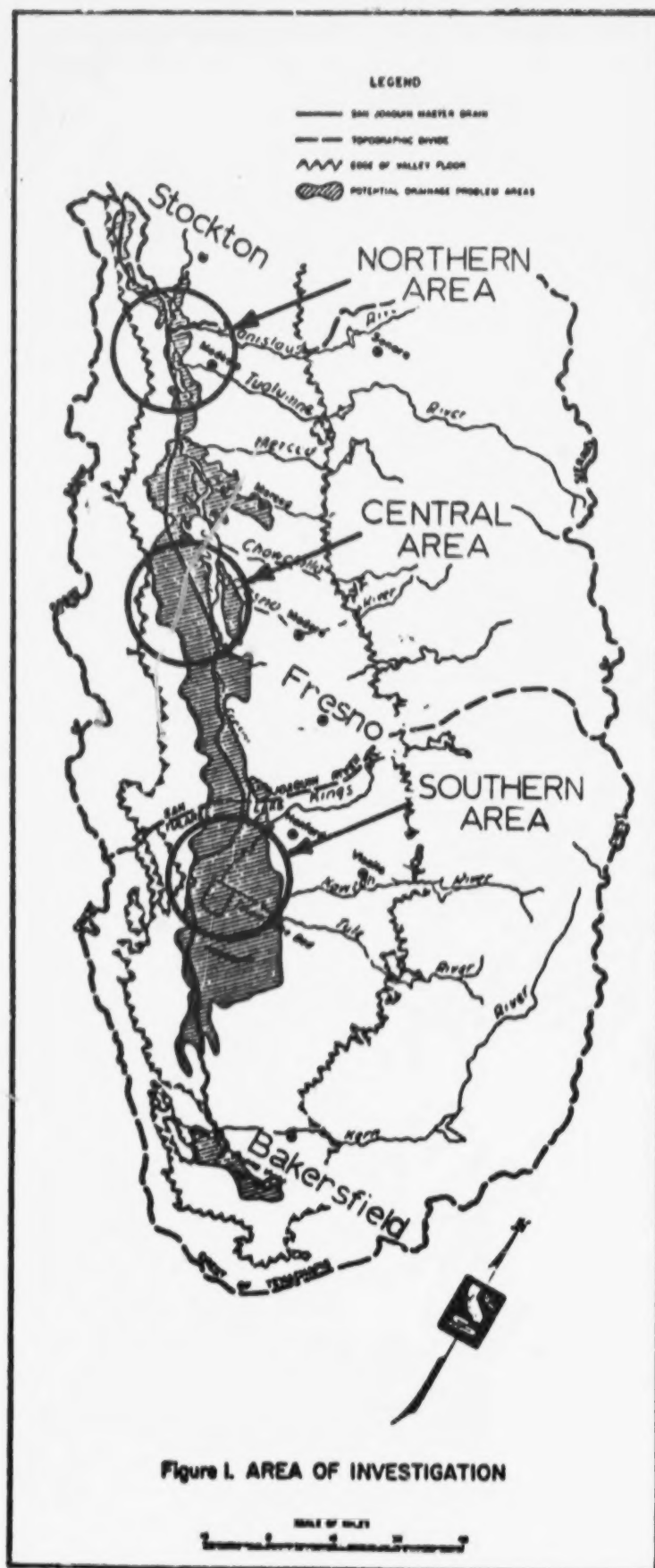


TABLE 1

SUMMARY OF TILE DRAINAGE MONITORING PROGRAM
BY AREA, PHYSIOGRAPHIC POSITION AND SOILS

Physiographic Position											
Recent Alluvium				Older Alluvium			Basin and Basin Rim			Total	
Soil Series	No. of Systems	Acres	Soil Series	No. of Systems	Acres	Soil Series	No. of Systems	Acres	No. of Systems	Acres	
Sorrento	6	2,360	Rincon Ambrose	4 3	395 169	Sacramento	1	73	14	3,497	
Panoche Panhill	8 4	2,071 595	Lost Hills	3	858	Oxalis Lethent Willows	4 2 1	825 390 140	22	4,879	
Foster	1	73		0	0	Tulare Hacienda	4 1	1,080 120	6	1,273	
Total		19	5,099	10	1,922		13	2,628	42	9,649	

area occupy only two physiographic positions. The soils are predominantly of the Tulare series. Agriculture in the southern area is not as diversified as the central area and has proceeded with reclamation of the lake bottom. Cotton, grain, and alfalfa are the main crops; large acreages are still fallowed in the area. Well-planned fertilizer programs are practiced by the larger farming operations.

Physiographic Positions

Older Alluvial Fans. This physiographic position consists of older alluvium resting at the higher elevations in which the soils are medium textured and have moderately developed subsoils (developed soils are soils which exhibit clay movement from the surface horizon and clay accumulation in the lower horizon). These older fans have developed from recent material in which the drainageways have been entrenched so there is seldom any deposition of new material on the surface. Weathering and soil development have caused the formation of well-defined soil layers.

Recent Alluvial Fans. Recent alluvial fans occur at lower elevations than the older alluvial fans. Soils have been deposited by recent flooding of intermittent streams from the older alluvium and parent soils at higher elevations. They are derived from outwash materials, mostly from sandstone and shale rocks and owe their characteristics largely to the character of the stratified parent material.

Basin. In this paper, basin and basin rim positions are included under the general category of basin. The basin is the lowest position elevationwise. Soils of the basin position are fine textured with slightly compact to compact subsoils and stratified at lower depths. Soils in basin positions are composed of colloidal materials alluviated from soils and parent materials at higher elevations.

Soils

In the northern area the soils in the recent alluvial fan positions are mostly of the Sorrento soil series which have medium to fine-textured surfaces and are highly stratified throughout the profile resulting in lateral water movement in some areas. The older fan position is dominated by Rincon soil series which is moderately developed with restricted vertical drainage in the subsoil. The Ambrose soil series is in the older position. The alluvium in this area appears to be eroded from Pliocene, Pleistocene, and Quaternary nonmarine formations.

Recent alluvial fans in the central area are dominated by the Panoche soil series which is highly stratified with silt, lime seams, and coarse material, resulting in lateral movement in some areas. The Panoche series is closely associated with the slightly more developed Panhill. The older alluvium is represented by the Lost Hills soil series which differs from the Panoche in having distinct profile development. The recent and older alluvium soils are derived from early Tertiary marine sediments of the coastal mountains. These soils are by nature highly calcareous, contain appreciable quantities of gypsum and are medium to fine textured on the surface. The soils of the basin are clays and clay loams which are predominantly from mixed granitic sources.

Most tile systems in the southern area are located in the basin position. The soils are predominantly of the Tulare soil series, a flat mass of fine alluvial material deposited by the Kings River. Large areas of these poorly drained soils have been reclaimed. These soils are derived mainly from igneous and sedimentary rock sources. They contain decayed remnants of lake vegetation and shell fragments of mollusks in the profiles and are calcareous throughout.

Soils and geological data were obtained from the U.S. Department of Agriculture Soil Conservation Service soil maps.

Selection of Tile Drainage Systems

Several factors were considered important in the selection of tile drainage systems for monitoring. A number of tile drainage systems were selected within each of the tiled areas. Larger systems capable of reflecting the flows and concentrations from large blocks of similar soils were preferred over smaller ones. Systems were selected from various physiographic positions and as many different soils as were available. Systems having a large number of rather closely spaced laterals were chosen instead of single-line type drains. Only tile drainage systems underlying fields having active irrigation and fertilization programs were selected.

Tile Drainage Systems

Figure 2 is a representation of a typical tile drainage system. Drains are buried 7 to 9 feet below the surface of the field and surrounded with a sand or gravel envelope. The drains either have open joints or are perforated. Flow within the drain is directed to a collector line at the edge of the field and then to a concrete reservoir, or sump, where it is then pumped into an open drain.

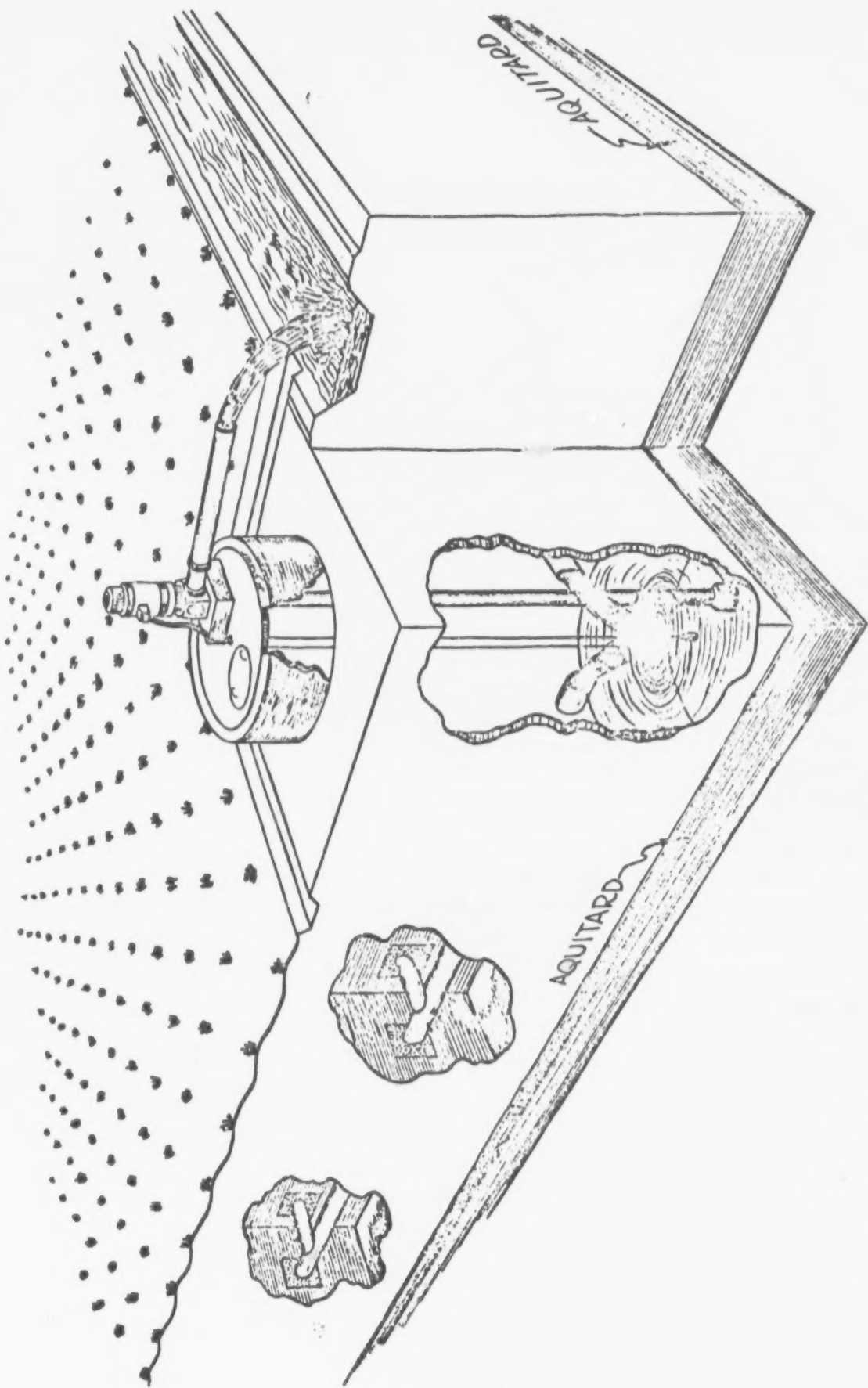


Figure 2
TYPICAL TILE DRAINAGE SYSTEM
WEST SIDE OF THE SAN JOAQUIN VALLEY

Tile systems are generally of two basic designs: (a) the interceptor type, a single line drain placed on the periphery of a field to intercept or reduce lateral movement of water; and (b) the relief type, having multiple laterals designed to alleviate existing high-water table conditions within a field.

Tile systems of the central area are mostly of the relief type with spacings that generally range from 200 to 600 feet. Northern tile systems are mostly of the interceptor type; laterals are added if a need arises. Tile drainage systems in the southern area consist of both types mentioned above.

Sampling

Flow rates and nutrient concentrations were initially determined hourly, daily, twice a week, and weekly until a reliable sampling frequency was determined. Only minor fluctuations of nutrient levels were observed for the different sampling frequencies; therefore, a schedule of weekly sampling was determined satisfactory for this investigation. Pesticide samples were collected quarterly from the three drainage areas. Precautions were exercised to minimize contamination. Soil samples were collected at depth increments of about 1 foot.

Analyses

Nitrate determinations were made using a cadmium reduction technique. The accuracy of this technique was determined to be adequate for this study through the use of standardization curves and redundant testing of 10 percent of the samples with the brucine technique. Nitrate analyses of soils were made on soil extracts, suction filtered from a saturated paste. Soils were extracted and refrigerated to minimize denitrification. A modified stannous chloride method was used for phosphate analyses. Electrical conductivities were determined with a conductivity bridge. Pesticide samples were analyzed using a microcoulometric gas chromatograph technique.

Calculations

Nitrate and phosphate values were converted to pounds of nitrate nitrogen and phosphate phosphorus per day, weighted by the average weekly flow, and summarized to give average values per system per month. These values were in turn summarized for different physiographic positions and soil series. Summaries of average flows and concentrations in the tables are weighted average values for the 2-year period.

Chlorinated hydrocarbon pesticide maximum, minimum, and average values were determined as well as the percentage of times detected. Average values were calculated assuming a zero concentration for samples in which no chlorinated hydrocarbons were detected. Averages were also calculated for only the samples in which chlorinated hydrocarbons were detected.

Nitrogen concentrations from 3- to 10-foot depths were averaged for purposes of soil profile analysis in this report.

Agricultural practices data were obtained from farmers and operators on fields which had the tile drainage systems that were sampled. The crop pattern and pesticide and fertilization data were obtained for a 10-year period (1958-1968).

Results of Drainage Monitoring Program

Wide variations were observed in tile drainage discharge and nutrient concentrations between the various systems monitored for any given time of year. The total annual discharge from individual systems ranged from a low of 0.3 to a high of 17.0 acre-feet per acre per year; average nitrogen and phosphorus concentrations ranged from 2 to 400 mg/l and 0.01 to 4.0 mg/l, respectively.

Seasonal variations of discharge were observed in all individual tile drainage systems monitored. Flows were the highest during the summer months (April-September) and decreased following a suspension of irrigation. Minor seasonal variations of nutrient concentrations were observed in drainage from all individual tile systems studied. Nitrogen concentrations in tile drainage from several rice fields declined rapidly during flooding and increased when the fields were drained. In tile drains sampled since 1959, annual average nitrogen concentrations have not declined.

Great differences in flows and nutrient concentrations were observed between some areas. The highest discharge rates were observed in the northern area where flows ranged from 0.05 to 0.03 acre-feet per acre per month during the summer season and averaged 1.8 acre-feet per acre per year for the 2 years investigated.

Nutrient concentrations were the highest in the central area where average values in the combined drainage ranged from 22 to 51 mg/l with an annual average of 33 mg/l.

Tile drainage from the southern area had an average phosphorus concentration which was three times that of any other area investigated. The overall average phosphate phosphorus of the southern

area drainage was 0.68 mg/l and ranged from 0.60 to 0.85 mg/l. Seasonal variation of flows for the different areas are illustrated in figure 3; nutrient concentrations are presented in figures 4 and 5.

Nitrogen concentrations also varied according to physiographic positions and soil series. Nutrient concentrations in drainage from older and recent alluvium of the central area was much higher than drainage from similar physiographic positions in the other two areas. The drainage from the basin position had the lowest nitrogen concentrations. The total flow and average annual nutrient concentrations for the systems monitored are summarized by area and physiographic position in table 2.

It is evident from the data that tile drainage from certain soils occupying alluvial fan positions contained substantially higher concentrations of nitrogen than did drainage from other soils situated in similar positions in other areas. The highest concentrations observed were in the drainage from the older and recent alluvium of the central area, where 15 tile systems located in three alluvial soils ranged from 35 to 53 mg/l and averaged 44 mg/l, which was better than four times that in drainage from soils in fan positions in the northern area. Table 3 shows the comparison of nutrient concentrations in tile drainage from all of the alluvial soils in the areas studied.

Soil Nitrogen Investigations

Certain alluvial soils of the west side of the San Joaquin Valley contain high concentrations of nitrogen in the subsoil. This phenomenon was first reported by Dyer (3) whose data showed that nitrogen concentrations exceeded 1,400 mg/l in Panoche soils down to 50 feet. Doneen (4, 5) also observed high nitrogen concentrations in shallow ground water in irrigated west side soils and in the profiles of virgin sites. These observations of higher than normal nitrogen values in the above investigations were responsible for a program to define areas of residual nitrogen and correlate the findings to those in tile drainage.

Soil profiles representing different soil series and physiographic positions were sampled in an area extending from Tracy south along the west side to Wasco. Forty-four sites were augered to a depth of 10 feet or more and samples were collected at 1-1/2-foot increments for nitrogen analysis. Virgin or unirrigated sites were sought to obtain the status of the quantity of the nitrogen in the soil before irrigation. Several dry farmed and irrigated sites were also sampled.

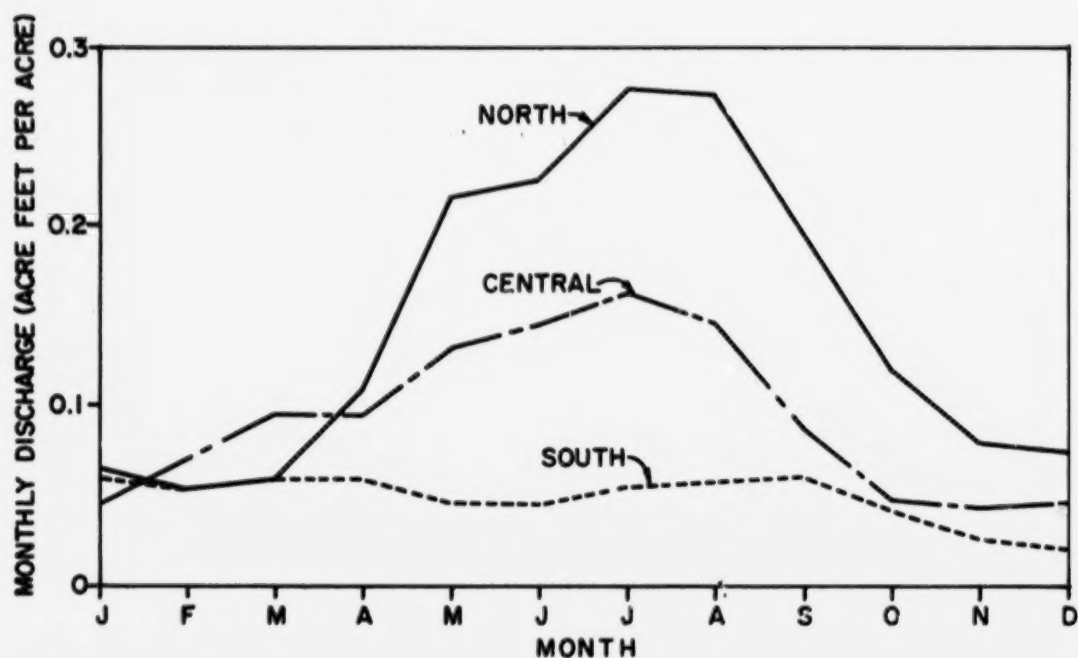


Figure 3 - SEASONAL VARIATIONS OF FLOWS FROM THE NORTH, CENTRAL AND SOUTHERN AREAS

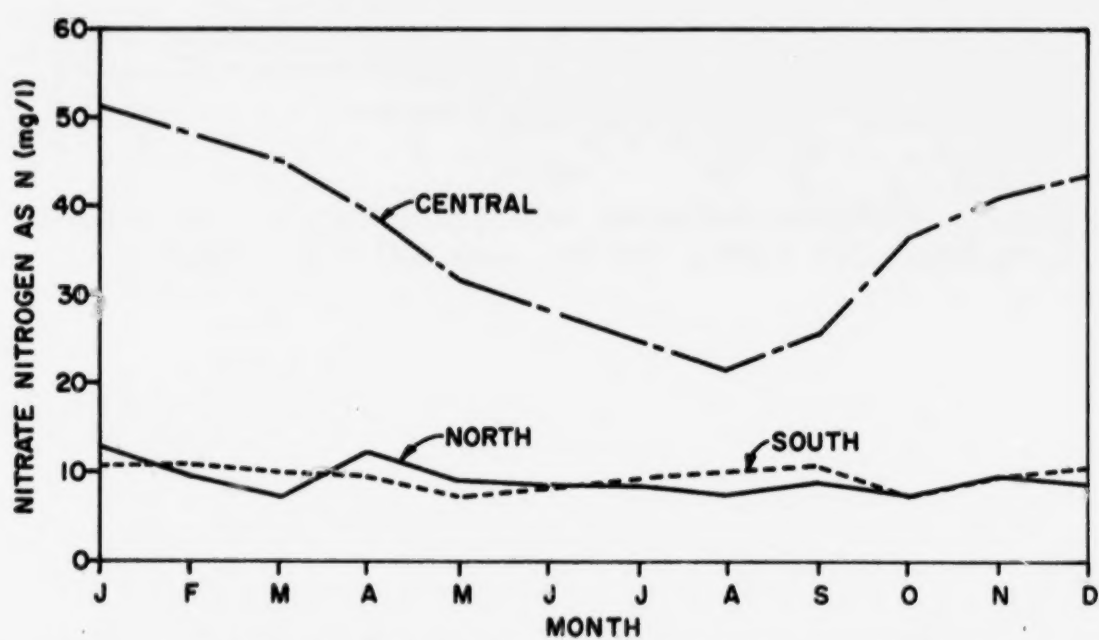


Figure 4- SEASONAL VARIATIONS OF NITROGEN CONCENTRATIONS FROM THE NORTH, CENTRAL AND SOUTHERN AREAS

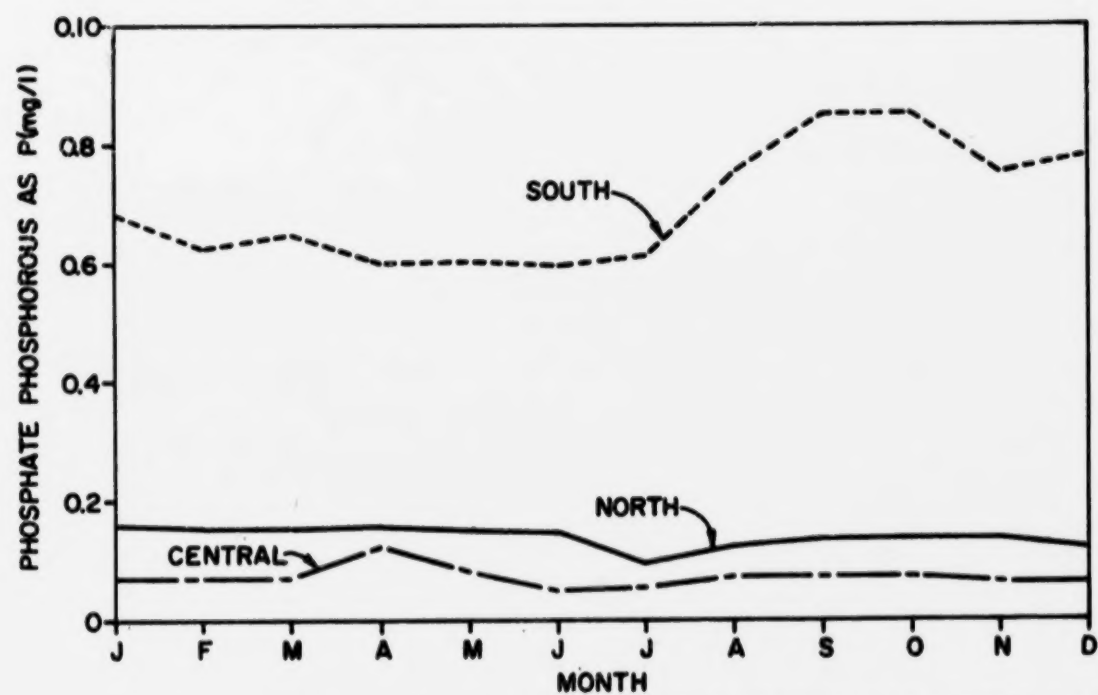


Figure 5 - SEASONAL VARIATION OF PHOSPHOROUS CONCENTRATIONS FROM THE NORTH, CENTRAL AND SOUTHERN AREAS

TABLE 2

TILE DRAIN FLOWS AND NUTRIENT CONCENTRATIONS
SUMMARIZED BY AREA AND PHYSIOGRAPHIC POSITION

	NORTH			CENTRAL			SOUTH			ALL AREAS		
	Total Flow (Ac. Ft./Yr.)	Avg. NO ₃ -N (mg/l)	Avg. PO ₄ -P (mg/l)	Total Flow (Ac. Ft./Yr.)	Avg. NO ₃ -N (mg/l)	Avg. PO ₄ -P (mg/l)	Total Flow (Ac. Ft./Yr.)	Avg. NO ₃ -N (mg/l)	Avg. PO ₄ -P (mg/l)	Total Flow (Ac. Ft./Yr.)	Avg. NO ₃ -N (mg/l)	Avg. PO ₄ -P (mg/l)
Recent Alluvium	5,042	10	0.07	5,382	42	0.06	109	14	0.70	10,533	26	0.08
Older Alluvium	5,823	8	0.08	1,168	53	0.06	N.T. ^{2/}	N.T.	N.T.	6,992	15	0.08
Basin ^{1/}	306	5	0.26	3,139	11	0.08	1,137	9	0.67	4,581	10	0.24
Summation	11,171	9	0.08	9,689	33	0.07	1,246	9	0.67	22,106	19.4	0.11

^{1/} Including basin rim soils.

^{2/} Physiographic position not represented by tile installations.

TABLE 3
COMPARISON OF NUTRIENT CONCENTRATIONS
IN TILE DRAINAGE FROM ALLUVIAL SOILS

		Physiographic Position					
		Recent Alluvium		Older Alluvium		Total	
		Soil Series	Avg. NO ₃ -N mg/l	Avg. PO ₄ -P mg/l	Soil Series	Avg. NO ₃ -N mg/l	Avg. PO ₄ -P mg/l
North	Area	Sorrento	10	0.07	Rincon	8	0.07
					Ambrose	7	0.09
Central	Area	Panoche	39	0.07	Lost Hills	53	0.06
		Panhill	45	0.05			
South		Foster	14	0.70			
Total			26	0.08		15	0.08
						44	0.06
						9	0.08
						14	0.70

Results of Soil Nitrogen Investigations

Older Alluvium Position Soils. Five profiles were sampled in the older alluvial fan position; these were of the Lost Hills series and were virgin sites. Nitrogen concentrations in the soil extracts ranged from 2 to 195 mg/l.

Recent Alluvial Position Soils. In the more recent alluvium six profiles of Panhill soils had nitrate concentrations ranging from 13 to 164 mg/l. All of the soils were virgin with the exception of one dry-farmed site. One soil which was low in nitrogen, 13 mg/l, was located in a well-drained area which suggests that leaching took place. The highest nitrogen values were observed at three Panoche sites which ranged from 32 to 231 mg/l. Two profiles of Sorrento were examined; one was dry farmed and the other virgin; concentrations were 17 and 25 mg/l respectively. Rincon soils were examined at two sites; one site averaged 3 mg/l and the other 13 mg/l. One profile of Ambrose was analyzed at 41 mg/l.

Twelve profiles of Panoche soils were investigated in irrigated areas to determine the effects of leaching upon the nitrogen in the soil. These sites were sampled by groups in different farmed areas along the west side. Seven profiles ranged from 7 to 16 mg/l; three profiles showed slightly higher concentrations, from 18 to 36 mg/l. Five of the sites were located within the interfan areas and ranged from 9 to 92 mg/l. Some of the soils examined in the interfan areas were on the average four times higher than those in the direct course of the depositing stream.

Basin Position Soils. Five virgin soils in the basin physiographic position had nitrogen concentrations ranging from 1 to 13 mg/l. Only two basin sites sampled were observed to have high nitrates in the soil profiles. This was an atypical area of severely restricted drainage where excessive salt had accumulated in the soil profile from soils at higher elevations. Nitrogen concentrations in drainage from an experimental tile system located in the same area ranged from 370 to better than 2,000 mg/l. This tile system was not included in the monitoring program.

Effects of Agricultural Practices

Historic cropping data reflected some changes in agriculture but were more important for determining trends in fertilization and estimates of water use. No attempt was made in this report to assess the amount of nitrogen contributed from crops or applied water. Average irrigation applications in all study areas were nearly the same according to records obtained from irrigation district offices in 1967. Precipitation was higher in the northern area.

Historically, the highest fertilization rates were recorded in the central area. In a few individual cases the concentrations observed in the tile drainage seemed to correlate with the amounts of fertilizer applied. Fertilizer records were obtained over a 10-year period to correlate applied nitrogen to the concentrations observed in the subsurface waters. Average fertilization for the major areas investigated are given below, along with the nitrogen discharged in the combined drainage.

Area	Applied Fertilizer as Lbs of N/Ac			Discharged Nitrate as Nitrogen	
	1967	1957-1962	1957-1967	Lbs/Ac	Concentration mg/l
North	72	51	42	35	9
Central	92	75	88	83	33
South	43	68	74	2	9

Amounts and concentrations of nitrogen in drainage from the central area seemed to correlate with applied nitrogen fertilizer. However, amounts not too different from that applied in the central area were applied in the southern and northern areas at different times with no observable effect on present concentrations.

Phosphate fertilizer was found to be applied sporadically in the northern and central areas; records were not kept on most farms. Records of its application were only obtained from one large operation in the southern area which indicated that phosphate fertilizer was applied regularly at the rate of 50 pounds per acre every other year.

Pesticides in Subsurface Agricultural Drainage

Over the years the greatest number of pesticide samples were collected in the central area. This was the area where the greatest number of pesticides were detected for the number of samples taken; the highest maximum values were also reported in this area (2,800 p.p.t.). Drainage waters from the southern area contained the highest average concentrations of chlorinated hydrocarbon pesticides. A summary of chlorinated hydrocarbon concentrations in agricultural drainage is presented in table 4. The averages of all tile drains investigated show that the highest concentrations occurred in 1963 and 1964 and declined each year until 1968, at which time chlorinated hydrocarbons increased slightly. These changes are shown in table 5. From 1963 through 1968, 371 samples were collected from tile drainage systems of which chlorinated hydrocarbons were detected 219 times or 59 percent of the total samples collected. The most frequently detected CHC compound was

TABLE 4

SUMMATION OF CHLORINATED HYDROCARBON
CONCENTRATIONS IN AGRICULTURAL SUBSURFACE DRAINAGE
WATERS OF THE SAN JOAQUIN VALLEY

Area	Time Sampled	Time Detected	Percent Time Detected	1963-1968		
				Maximum	Minimum	Average
North	70	29	41	215	0	19
Central	216	150	69	2,300	0	96
South	92	38	41	1,175	0	113
Total	378	217	57	2,800	0	86
						46
						138
						274
						150

1. Average values include 0 values when chlorinated hydrocarbon was not detected.

2. Average values include only the detected chlorinated hydrocarbon.

TABLE 5 - SUMMATION OF CHLORINATED HYDROCARBON
INSECTICIDES CONCENTRATIONS OBSERVED IN AGRICULTURAL
SUBSURFACE DRAINAGE OF THE SAN JOAQUIN VALLEY

Year	Times Sampled	Times Detected	Percent Times Detected	Maximum	Minimum	Avg. Conc. 0-values (ppt) ¹	Avg. Conc. Det-values (ppt) ²
1963-64	16	15	94	2800	0	382	406
1965	50	48	96	1100	0	189	197
1966	105	78	74	1175	0	112	146
1967	121	48	40	320	0	16	44
1968	79	30	38	543	0	40	105

¹ Average values include 0 values when chlorinated hydrocarbons were not detected; parts per trillion.

² Average values include only the detected chlorinated hydrocarbons; parts per trillion.

DDD/DDT. Out of 452 total detections, it was detected 156 times or approximately 34 percent of the time. Toxaphene was found in greater concentrations than any other compound. A table showing the most frequently detected CHC compounds and their maximum, minimum, and average concentrations is given in table 6.

Usage

Records of acreages treated with various pesticides in Kern County strongly indicate a decline of the usage of chlorinated hydrocarbon pesticides and an increase in the use of organic phosphates and carbamates. The percentage of total acres treated with CHC-type insecticides generally decreased from 1948 to 1968. The inverse is true of organic phosphates which increased steadily for the same period. According to the data, the use of organic phosphates surpassed CHC-type compounds in 1965. Trends in the usage of synthetic insecticides within Kern County is illustrated in figure 6.

Farm advisors of other counties contacted by the Department of Water Resources personnel reported decreased usage of CHC compounds within their respective counties. Pesticide production records (6) also correlate with the Kern County findings.

Discussion

Flows. Variable rates of discharge in tile drainage systems are attributed mainly to irrigation. Flooded rice fields were a striking example of irrigation influence; flows increased during the summer months in all tile drains investigated. Soil stratigraphy is a doubtless influence in most alluvial soils of the west side; lateral water movement is common knowledge to most conservationists and drainage specialists. Two tile drains in the northern area obviously discharged more water than was applied; flows from these systems coincide with measurements and reported flows of other known drainage systems not included in the study. Vast areas of stratified alluvium along the west side have been classified by the Soil Conservation Service (7) as having soil horizons where the horizontal exceeds the vertical hydraulic conductivity. Also, old meandering streamways long since obliterated by man's activity form an inextricable network of natural aquifers in the recent alluvial fans which "pinch off" as they approach the basin soils.

Nutrients in Tile Drainage. Nitrogen in tile drainage was found to be more closely associated with the physiographic positions than agricultural practices. Several meaningful relationships were established between the amount of nitrogen found in the soil profiles and that discharged in similar soils by tile drainage systems.

TABLE 6

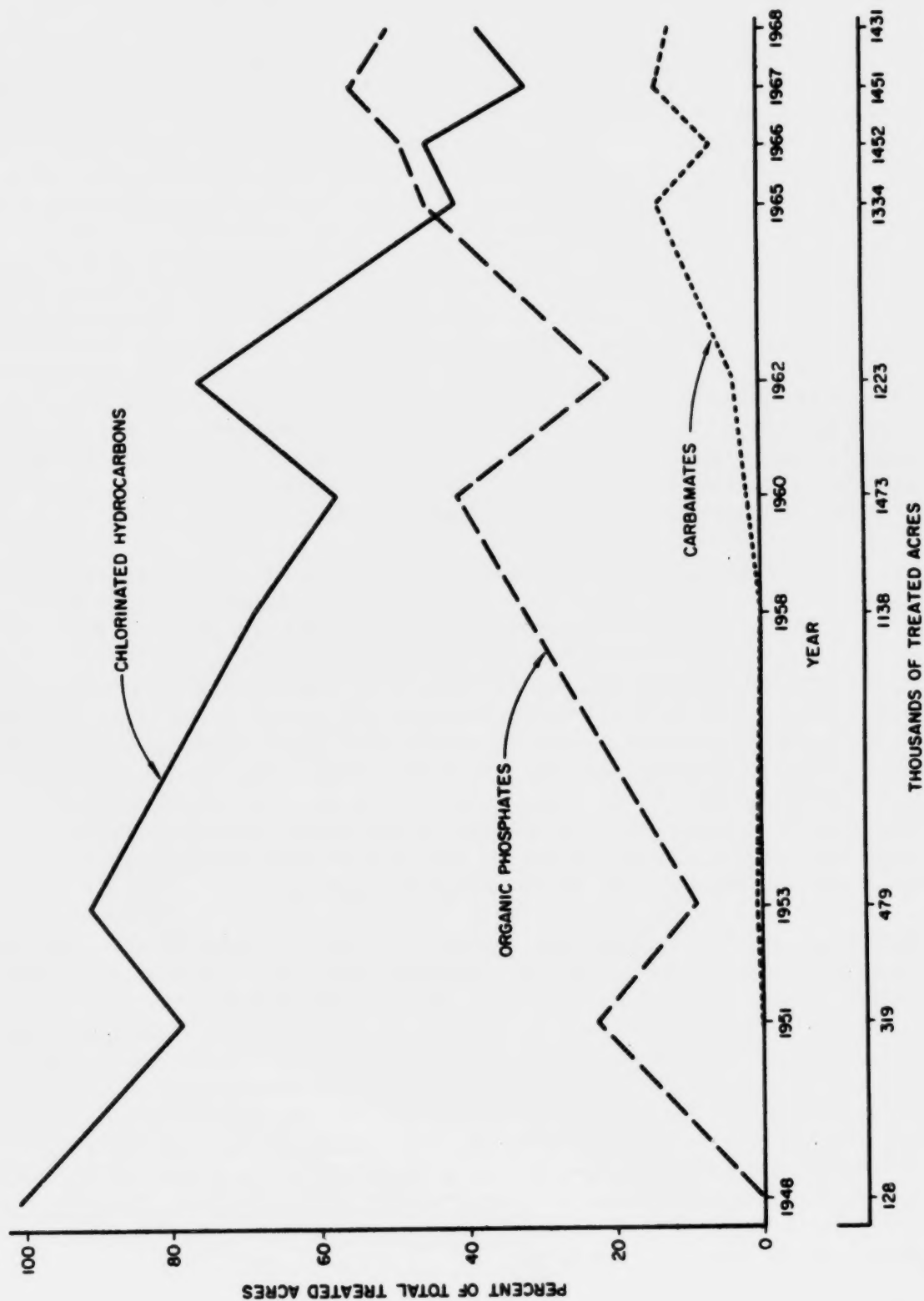
CONCENTRATIONS OF MOST FREQUENTLY DETECTED
CHLORINATED HYDROCARBON PESTICIDES IN AGRICULTURAL
SUBSURFACE DRAINS IN THE SAN JOAQUIN VALLEY
(1963-1968)

CHC Compound	: Times : Detected	: Maximum : (ppt)	: Minimum : (ppt)	Averages	
				: O-values ^{1/}	: Det-values ^{2/}
DDD/DDT	156	600	0	22	53
Dieldrin	82	142	0	6	28
Toxaphene	44	950	0	44	369
DDE	41	130	0	2	20
Heptachlor Epoxide	39	45	0	1	13
Lindane	36	340	0	3	26
BHC	28	1500	0	6	81

^{1/} Average values include 0 values when chlorinated hydrocarbons were not detected.

^{2/} Average values include only the detected chlorinated hydrocarbons.

Figure 6. TRENDS IN THE USAGE OF SYNTHETIC INSECTICIDES WITHIN KERN COUNTY



1968 DATA ADDED MAY 5, 1969

Nitrogen concentrations varied greatly between individual tile drainage systems, depending upon the physiographic position and soil series in which the tile systems were located.

Soils of Alluvial Fan Positions. Great differences in nitrogen concentrations were observed in the combined drainage from alluvial soils in different study areas. Tile drainage in the northern area was, according to the data, four times lower in nitrogen than the alluvial soils of the central area. These vast differences were attributed to high residual nitrates in central area alluvial soils.

Tile systems associated with Panoche, Panhill, and Lost Hills soil series had high nitrogen concentrations in the tile drainage which correlated with the average concentrations found in virgin tile zones of the same soil series located higher on the alluvial fans. These high levels of residual nitrogen can possibly be attributed to nitrate-bearing parent material in the general area which consists mainly of sandstones and shales from sedimentary marine formations of the coastal range. Sorrento and Rincon soils, which according to the data are much lower in residual nitrogen, are derived from mixed marine and nonmarine sediments.

Profiles of irrigated alluvial soils in the central area contained lower levels of nitrogen than the virgin sites and the nitrogen concentrations varied considerably from place to place. Pierce, et al. (8), showed variable concentrations within a tile-drained field of the Panoche series in the study area. Variable concentrations in the soil profiles between irrigated areas are attributed to different leaching patterns associated with variable textures. Soil profiles sampled in the interfan areas were on the average four times higher in nitrogen than those in the direct course of the depositing stream. In general, the finer-textured alluvial profiles in the irrigated areas contain higher concentrations of nitrogen in the soil than coarser-textured soils.

Soils of the Basin Position. Lower concentrations of nitrogen were observed in drainage from tile systems located in basin and basin rim positions which correlated with the low values found in soil profiles. Average nitrogen concentrations in tile drainage ranged from 4 to 20 mg/l which correlated closely with the 1 to 13 mg/l in the soil tile zone. Field investigations conducted by the Federal Water Pollution Control Administration (8) in an area of oxalis soil (basin rim position) showed that nitrogen in soil moisture extracted at 1-foot intervals to a depth of 4 feet was on the average lower than that of three alluvial soils investigated. Tile drainage from the same field correlated very closely with the values observed in the soil profiles.

The causes of low concentrations of nitrogen in drainage from basin soils is unknown; however, vertical movement of surface water is restricted by the clay and clay loam profiles allowing better plant usage of nitrogen after fertilization. Denitrification losses in basin soils with high water table conditions are indicated by the presence of low nitrates in the subsoil and tile drainage waters of heavily fertilized fields.

Ponnamperuma (9) reports that after fertilization no more than 3 milligrams per liter had ever been reported in submerged soils, and that denitrification losses were offset by the use of ammonia type fertilizers. He concludes that nitrate is not a suitable fertilizer for rice because of denitrification and leaching processes. Power (10) reports bacterial denitrification losses may account for a major part of fertilizer nitrogen applied in lands with poor drainage. His beliefs are supported by Woldendorp (11) who reports that rapid denitrification occurs in well-drained soils during periods of intense root activity such as under a grass sod.

Tile drainage from flooded rice fields in the Firebaugh area showed decreases of nitrogen in some cases of less than one-third their wintertime concentrations. One field in particular dropped from 63 mg/l in January to 7 mg/l for the months of May, June, and July. Pierce, et al. (8), reports evidence of denitrification in Panoche and Tulare loam soils studied in laboratory lysimeters.

Fertilization. Lysimeter investigations (12) have shown that nitrogen leached through soils is quite variable depending upon the texture of the soil, the type of crop, and its maturity. Dyer, et al. (3), showed evidence of nitrate leaching due to irrigation in Panoche soils of the west side of the San Joaquin Valley; Johnston, et al. (13), reported an average concentration of 25.1 mg/l from intensified investigations of four tile drainage systems near Firebaugh, California. They also concluded that nitrogen and phosphorus losses correlated with fertilizer application in the fields investigated.

No direct correlations could be made between the applied fertilizer and the concentration of nutrients in tile drainage during this study. A general relationship appears to exist in the central area where the heaviest fertilization occurred and the greatest amounts of nitrogen were discharged; however, this was not considered conclusive. Records from the southern area indicate that the basin soils received greater quantities of phosphate type fertilizers in comparison to the other areas which again seems to indicate a relationship due to the fact that the highest phosphorus in tile drainage was discharged from that area. There may be other factors contributing to the complexity of the problem such as those observed

during soil investigations (14) in the lakebed. Samples of soil have shown there may be an association between shell fragments in the soil of the Tulare soil series and the extraordinary phosphorus content in the tile drainage. An analyses of shell fragments disclose 0.11 percent P_2O_5 by weight. Colormetric tests indicated 0.12 to 0.15 percent phosphate. Also, high water table conditions in the area promote anaerobic conditions in the soil as evidenced by the odor of H_2S gas in freshly augered holes, which may cause a release of phosphorus due to fluctuations in pH values.

Summary and Conclusions

Summary. Wide variations in flows and nutrient concentrations were observed between individual drainage systems for any given time of the year. Average concentrations of nitrogen and phosphorus ranged from 2 to 400 mg/l and 0.01 to 4.0 mg/l respectively. Large seasonal variations of tile drainage discharge were observed in all areas and were attributed mainly to irrigation. Tile drainage systems in the northern area discharged the greatest amounts of effluent at 1.8 acre-feet per acre per year.

Nitrogen concentrations were the highest in combined drainage from the central area; the average annual concentration was 33 mg/l; seasonal variation ranged from 22 to 51 mg/l.

Higher than normal concentrations of phosphorus were observed in the tile drainage from the southern area; the seasonal concentrations ranged from 0.60 to 0.85 and averaged 0.68 mg/l. However, on the average, nitrogen concentrations in the area were low.

Comparison of tile drainage from different physiographic positions showed that recent and older alluvial soils were higher in nitrogen than basin soils. The average concentrations of composited drainage from recent, older, and basin positions was 26, 15 and 10 mg/l respectively.

Great differences were observed in drainage from different alluvial soils in the area studied. Drainage from three alluvial soils, Panoche, Panhill, and Lost Hills, average 44 mg/l compared to 9 mg/l for the alluvial soils in the northern area.

Average nitrogen concentrations within samples of virgin profiles correlated very closely with tile drainage from tile-drained fields of the same soil series. Fertilizer application was higher in the central area; data show a slight increased usage of fertilizer over a 10-year period. The quantity of nitrogen in tile drainage seldom correlated with the amounts applied.

Chlorinated hydrocarbon pesticide concentrations have decreased in tile drainage from all areas investigated for the last 6 years. The number of times chlorinated hydrocarbons were detected also declined for the same period. Pesticide use records from Kern County showed definite decreases in usage of chlorinated hydrocarbons in favor of organic phosphates.

Conclusions

a. Variations in nitrogen concentrations of tile drainage are more dependent upon the physiographic position and soil series than all other factors.

b. High residual nitrates found in soils account for greater quantities of nitrogen in tile drainage than that contributed by fertilizers.

c. Decreasing concentrations of chlorinated hydrocarbon pesticides in tile drainage is attributed to a decline in usage.

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DESALINATION OF IRRIGATION RETURN WATERS

By

Bryan R. Sword¹

Introduction

Experiments were conducted from June 1967 to November 1968, on the desalination of agricultural tile drainage waters at the Interagency Agricultural Waste Water Treatment Center (IAWWTC) near Firebaugh, California. These experiments were conducted by the Federal Water Pollution Control Administration (FWPCA) in cooperation with the Office of Saline Water (OSW). The purpose of the study was to determine the technical feasibility of desalination of irrigation return waters. The units used were an Aerojet-General Reverse Osmosis Water Purifier Model 1-560B-1 and an Ionics Electrodialysis Demineralizer Model 300-B-3 (figures 1 and 2).

Water Quality

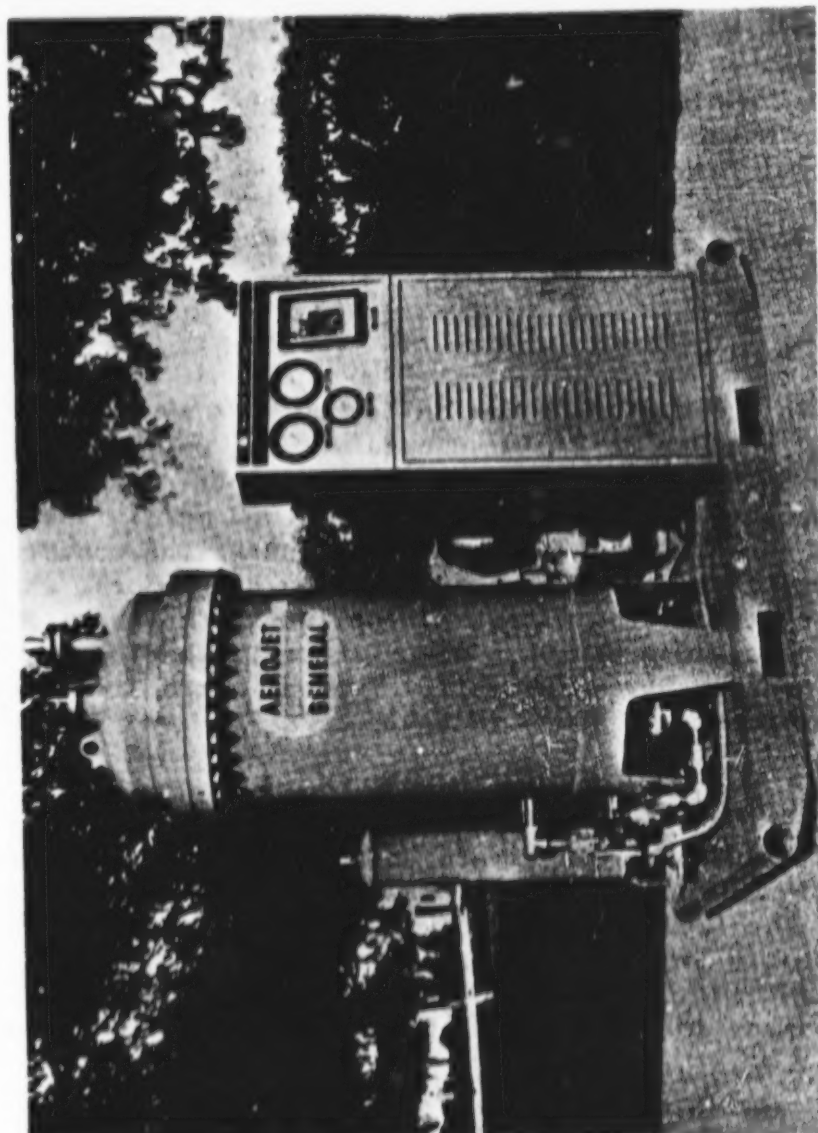
The water used in these studies was collected by a system of tile drains servicing a 400-acre field. These waters, which have percolated through 5 to 9 feet of soil, contained a total dissolved solids (TDS) concentration of from 2,500 to 8,000 mg/l. The variation in TDS was seasonal with the lower concentrations occurring during the summer growing season (June through September), when a large quantity of irrigation waters is applied to the land. Conversely in the nongrowing seasons, when little irrigation is done, the higher TDS concentrations prevail. Typical common ion analysis for these two extremes are shown in table 1.

TDS Control

For the initial portion of the experimentation (June 1967 to January 1968) the desalination process was operated using the tile drainage as it came from the fields. This, of course, gave an influent which varied greatly over the test period. This variance complicated data evaluation; therefore, a blending system was installed in June 1968 to provide a constant 3,000 mg/l TDS concentration.

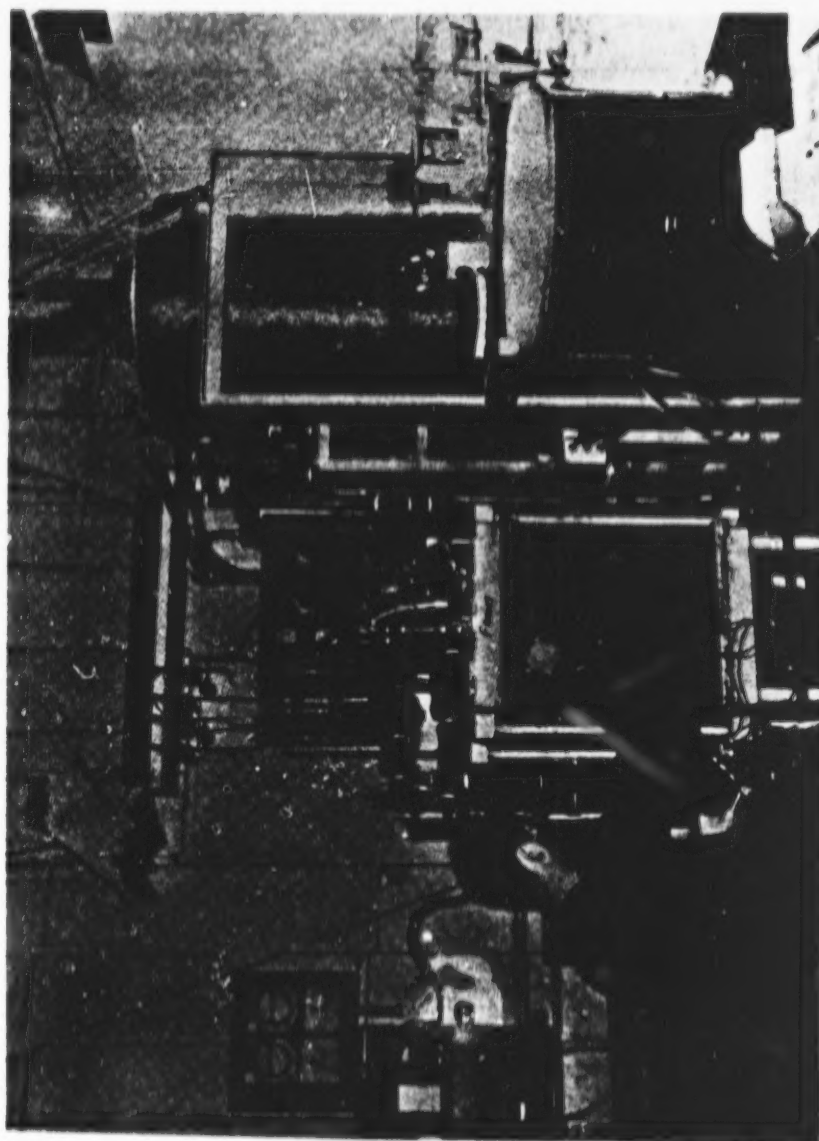
¹ Sanitary Engineer, San Joaquin Project, Federal Water Pollution Control Administration, U. S. Department of the Interior, Fresno, California.

FIGURE 1



AEROJET GENERAL
REVERSE OSMOSIS WATER PURIFIER
MODEL I-5608-1

FIGURE 2



IONICS ELECTRODIALYSIS DEMINERALIZER
MODEL 300-B-3

TABLE

DESALINATION OF IRRIGATION RETURN WATERS
CHEMICAL ANALYSIS OF HIGH AND LOW VOLUME FLOWS

	Low Volume Flows mg/l	High Volume Flows mg/l
Calcium	363	172
Magnesium	178	91
Sodium	1380	706
Potassium	4.0	3.8
Carbonate	0	22
Bicarbonate	462	437
Sulfate	3480	1520
Chloride	474	254
Nitrate	83	23
Boron	14	6.9
Iron (total)	0.03	0.10
pH*	8.3	8.6
TDS	6450	3020

* pH at time of analysis.

Reverse Osmosis

Unit Description and Pretreatment. The Aerojet-General Reverse Osmosis (RO) Unit Water Purifier Model 1-560B-1 has a plate and frame design and contains 600 square feet of membrane. The water flow schematic is shown in figure 3; the flow through the circular desalination plates is shown in figure 4.

The pH of the influent was lowered from approximately 7.4 to a range of 5.5 to 5.8 to control calcium carbonate precipitation and scaling. A calcium sulfate precipitation inhibitor was also used. Cyanamer P-35 manufactured by the American Cyanamid Company was used for this purpose. It was injected at a rate of 3 mg/l.

Membrane Characteristics. Two RO membrane stacks were studied. The first was a high pressure, low product yield, high salt rejection membrane. It was designed to have an applied pressure of 750 p.s.i.g. The second was designed to operate with a lower applied pressure (350 p.s.i.g.) and higher product yield; but with lower salt rejection characteristics.

Stack I. As shown in figure 5, the initial stack received an influent with a varying TDS from June 1967 to January 1968. This stack was subjected to the operational problems which occur during the startup of any experimental operation. However, for the initial 3 months it consistently produced a product containing under 500 mg/l of TDS, with an average salt rejection of over 90 percent (figures 6 and 7). A typical analysis for this performance of the unit's influent, product, and brine stream is shown in table 2. During the unit's operation, the product salinity fluctuated as the influent salinity varied. This variation is normal because of the increase in TDS concentration being passed through the membrane by pore transport. However, the continued decrease in product quality, as shown by figure 6, was due to biological fouling and subsequent membrane deterioration.

The flux rate (figure 8) for this stack was as high as 13 gallons per square foot of membrane per day. This occurred on the first day of operation. It declined throughout the experimental period with the exception of October 1967, when a higher than normally applied pressure was used. The flux rate decrease was caused partially by the increase in osmotic pressure due to the influent TDS increase. However, the degree of flux drop that did occur is probable due in part to another factor. It is speculated that with the high pressure at which the stack was operated, a separation occurred between the membrane and the spiral flow baffle (figure 4), thereby decreasing the exposure time of the water to the membranes and thus resulting in a lower flux rate. Table 3 summarizes the flux rates and salt rejection for the operation of Stack I.

AEROJET GENERAL REVERSE OSMOSIS - FLOW SCHEMATIC
NO SCALE

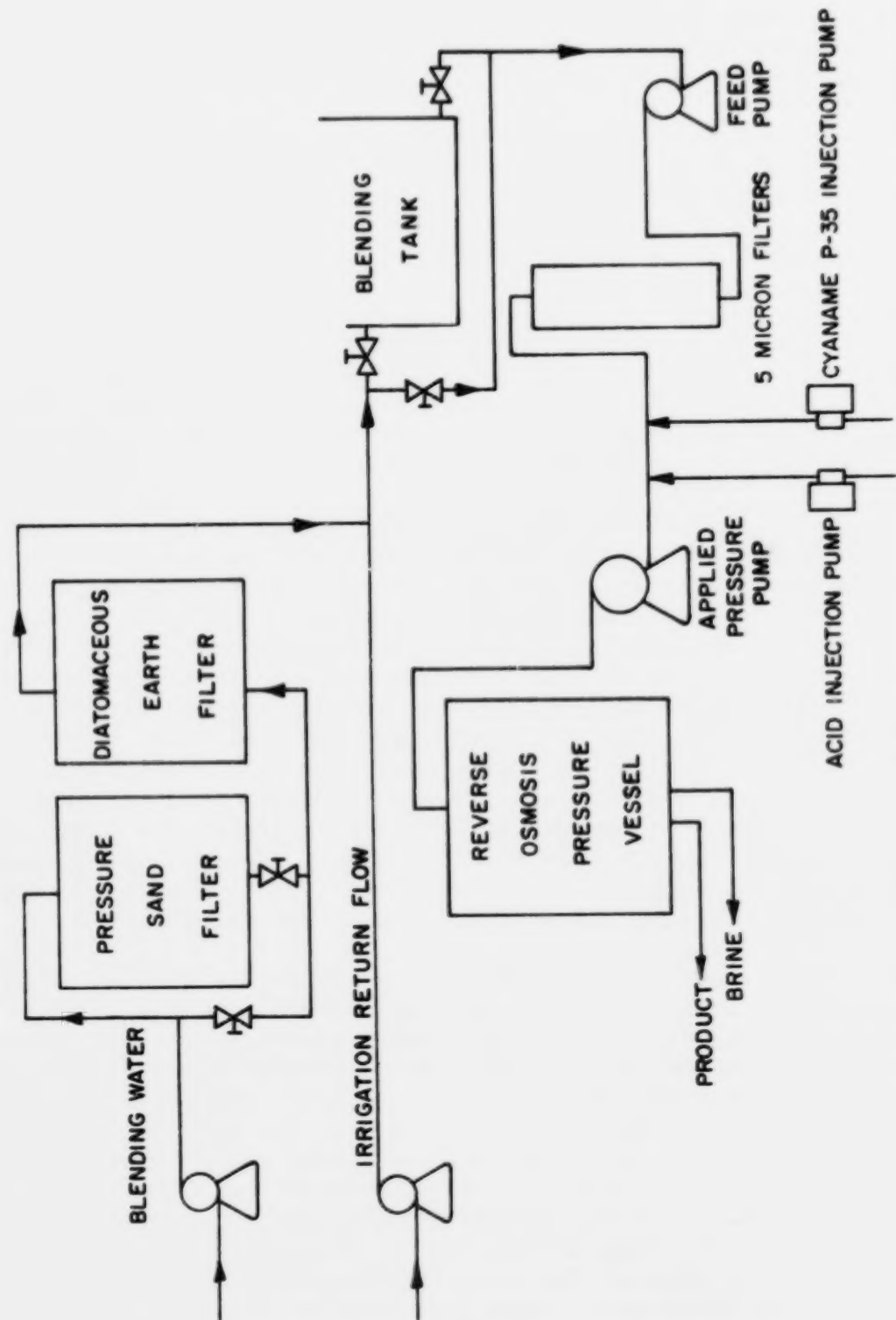


FIGURE 3

FIGURE 4

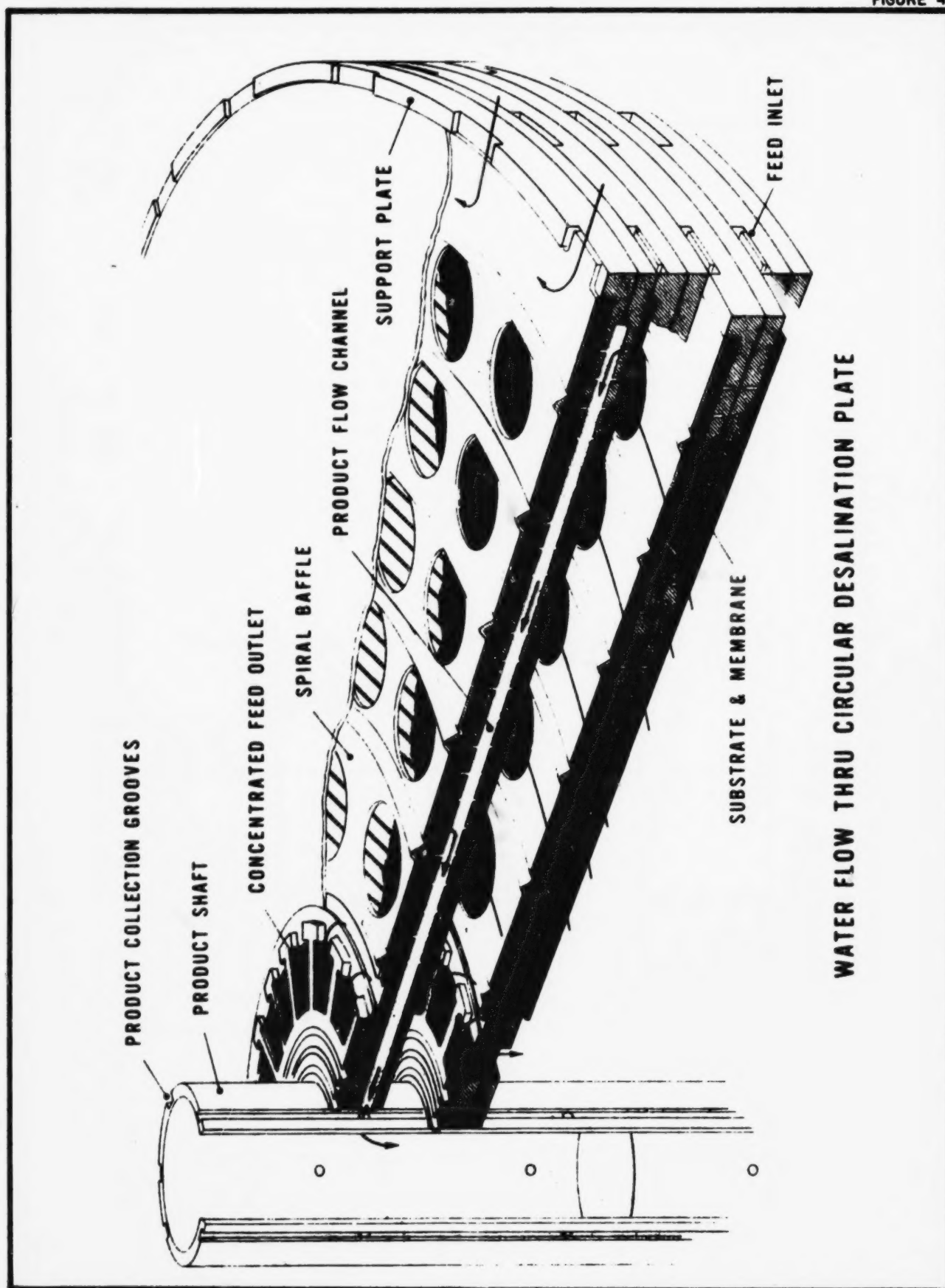
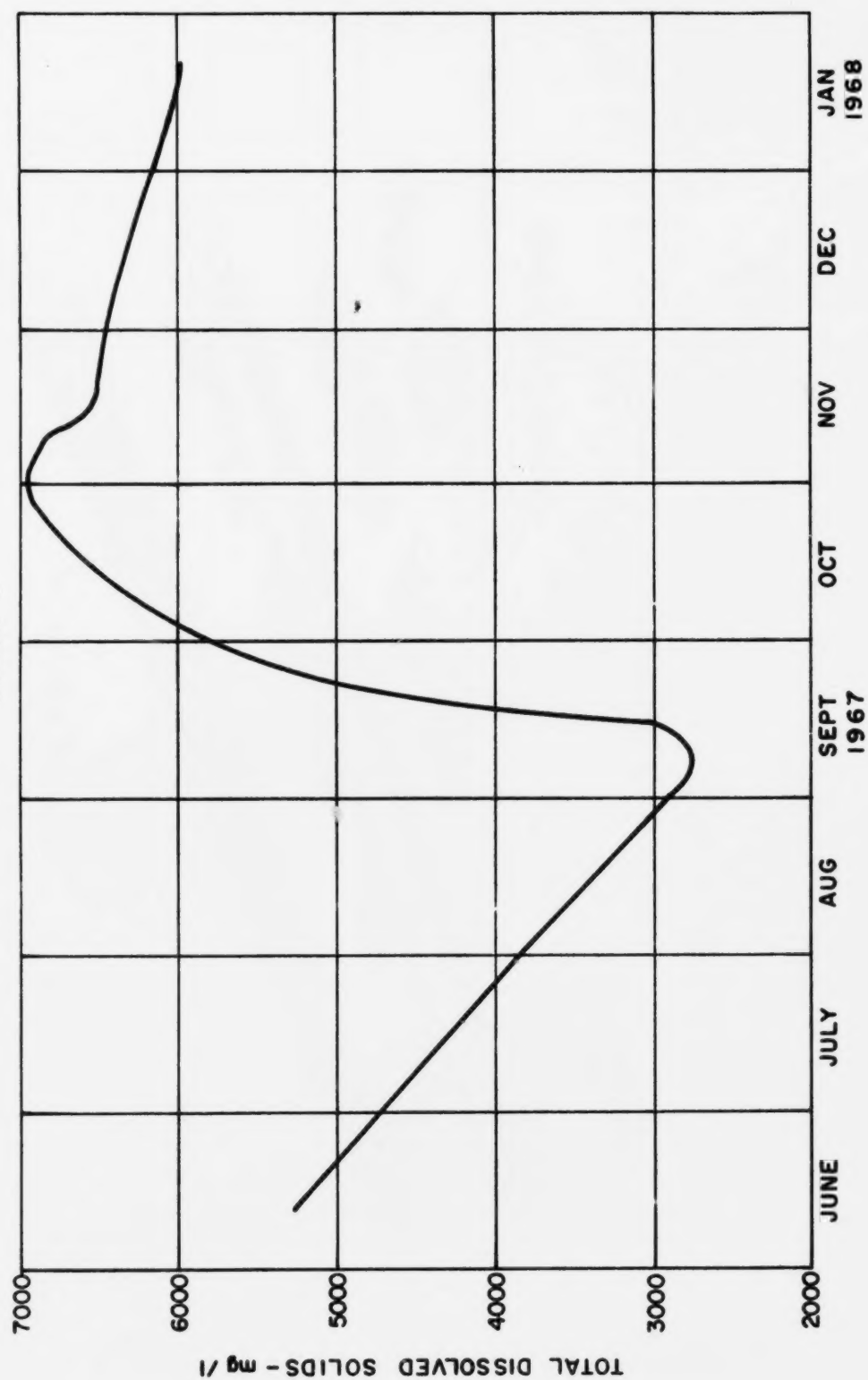


FIGURE 5

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
 IAWWTC - FIREBAUGH, CALIFORNIA
 REVERSE OSMOSIS DATA
 INFLUENT TOTAL DISSOLVED SOLIDS VERSUS TIME

STACK I



FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
 IAWWTC - FIREBAUGH, CALIFORNIA
 REVERSE OSMOSIS DATA
 PRODUCT TOTAL DISSOLVED SOLIDS VERSUS TIME

STACK I

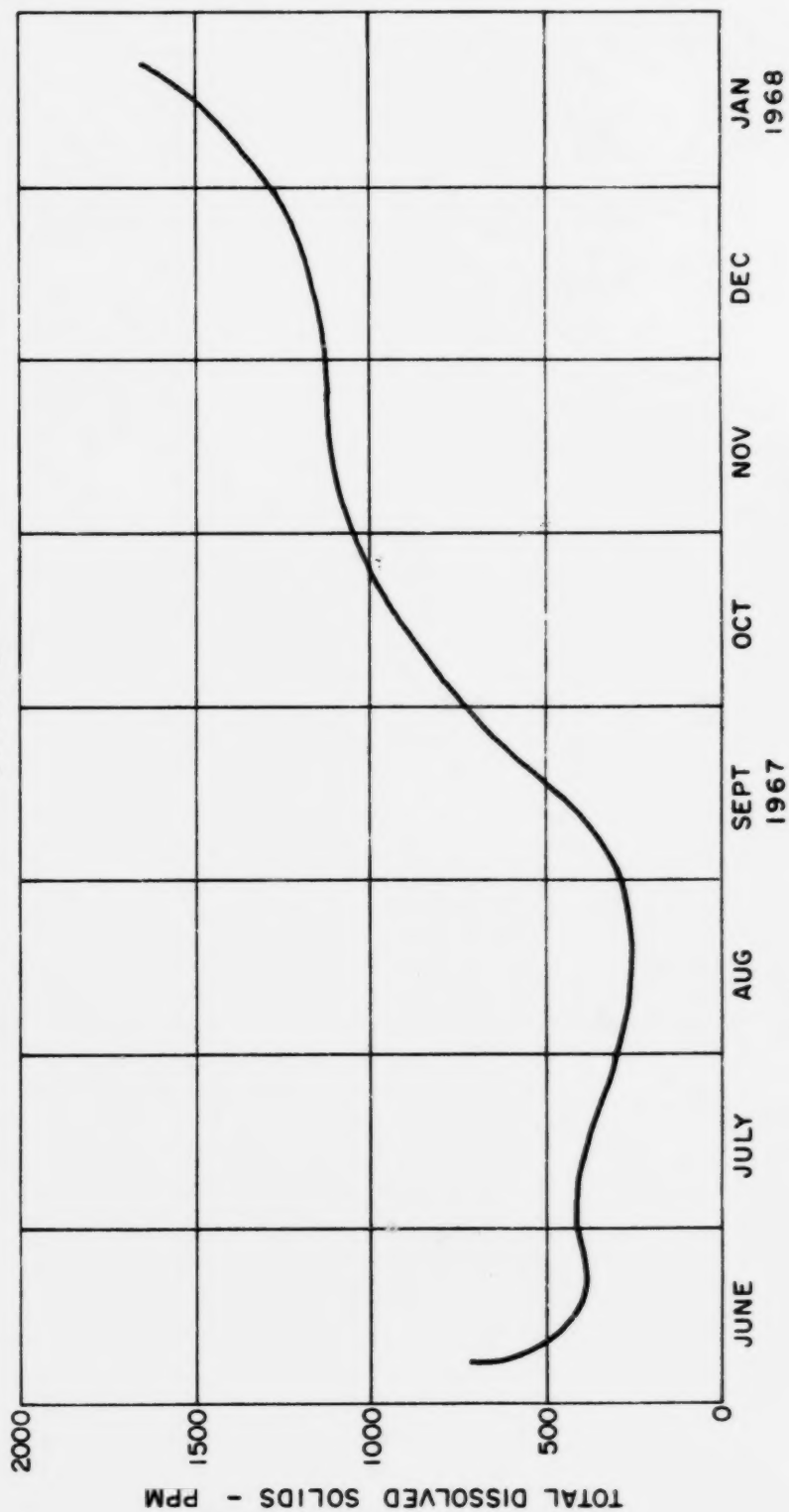


FIGURE 6

FIGURE 7

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
IAWWTC - FIREBAUGH, CALIFORNIA
REVERSE OSMOSIS DATA
PERCENT REMOVAL OF TDS VERSUS TIME

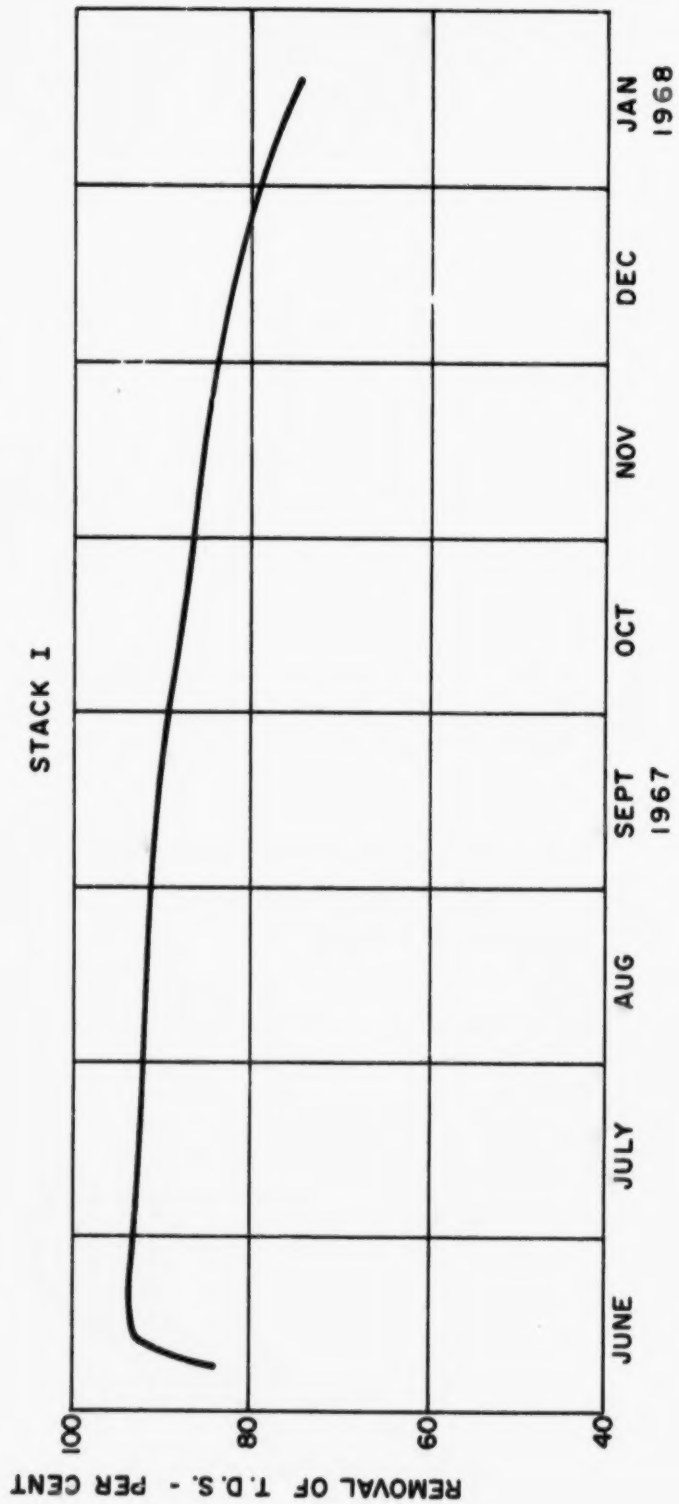


TABLE 2

REVERSE OSMOSIS
Stack I
Mineral Analysis

Operating Conditions

Date of Sample - July 14, 1967
Operating Pressure, psig - 750
Temperature of Feed Water - 77°F
pH of Feed Water - 5.5

Ion	PPM		
	Feed	Product	Brine
Ca ⁺⁺	230	3.3	347
Mg ⁺⁺	111	1.7	215
Na ⁺	862	82	1350
K ⁺	3.4	0.0	5.1
B	8.2	6.1	8.4
SO ₄ ⁼	2360	28	3720
HCO ₃ ⁻	98	16	140
Cl ⁻	314	94	440
NO ₃ ⁻	34	29	37
Fe (total)	0.02	0.02	0.02
SiO ₂	42	13	58
Total Alkalinity	80	13	136
Total Hardness	1030	15	1750
T.D.S.	4230	304	6400
pH*	6.4	5.4	6.5

* pH of samples at time of analysis.

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
 IAWWTC - FIREBAUGH, CALIFORNIA
 REVERSE OSMOSIS DATA
 PRODUCT FLUX VERSUS TIME

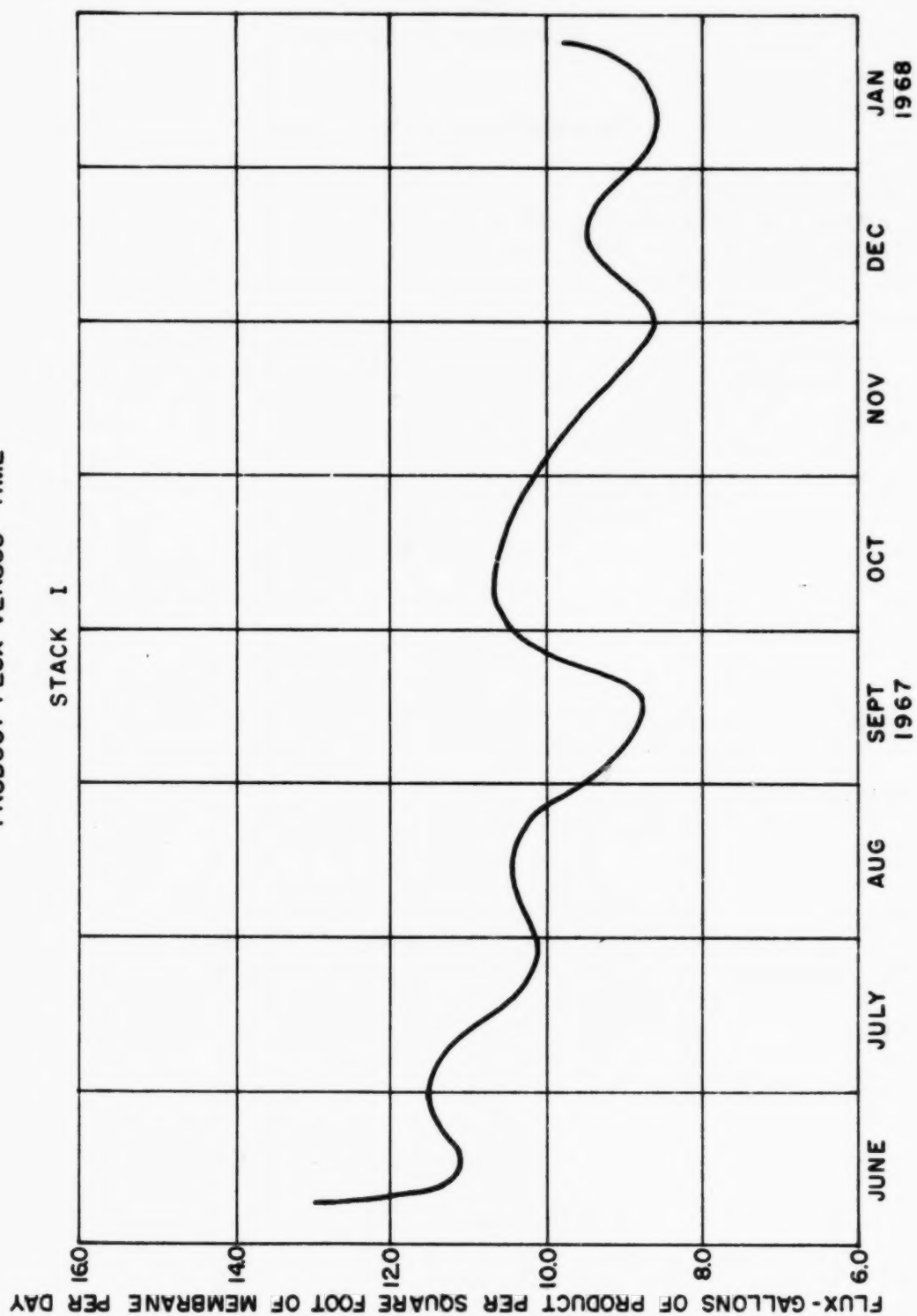


FIGURE 8

TABLE 3

REVERSE OSMOSIS
Stack I
Monthly Averages

Month	Flux (gal/ft ² /day)	Salt Rejection (percent)	Feed Salinity (ppm)	Product Recovery (percent)
June	11.2	92	5000	37
July	10.8	92	4300	37
August	10.3	92	3400	37
September	9.4	89	3900	37
October	10.2	86	6600	33
November	9.4	83	6650	36
December	9.1	82	6300	38
January	8.7	78	6000	40

Nitrate and boron removal rates are of particular interest. The nitrate removal rate varied considerably having a range of 0 to 49 percent removal with an average of 27 percent. Boron removed had a range of 8 to 35 percent removal with an average removal of 21 percent. Both ions were removed at a rate substantially lower than the general TDS removal rate.

Stack II--Operation and Performance. The second stack was in operation less than 3 months. Although spared the startup problems the previous stack experienced, an error in assembly shortened its life considerably. This stack was operated with the TDS blending system previously described. It received a more consistent influent with a TDS concentration of approximately 3,000 mg/l (figure 9). The unit's salt rejection remained constant at 85 percent with a product TDS between 400 and 600 mg/l (figure 10). Product flux, however, as seen in figure 11, varied widely. The variations occurred with constant operating conditions and were apparently independent of any exterior operational changes. Upon disassembly of the stack, it was found that blockages had occurred in the brine flow paths on the desalination plates. These blockages, the result of a corroded aluminum washer, caused an increase in the differential pressure of from 35 p.s.i.g. to above 95 p.s.i.g. through the stack. This reduced the effective pressure by 20 percent, which directly influenced the flux rate. It is also postulated that the effective membrane area of the unit was reduced by bridging of the spiral flow path with precipitated salt due to the closed brine stream. This would, as in the case of Stack I, result in a reduced exposure of the water to the membranes and again a decrease in product flux.

Due to the lower salt rejection design criteria of this stack, its nitrate and boron removal was essentially zero. All analyses indicated zero nitrate removal and a maximum boron removal of less than 0.5 percent. A typical influent, product, and brine stream analysis for this stack is presented in table 4.

Cost Analysis. The power, chemicals, and supply costs for Stack II were summarized in an internal report to Office of Saline Water. The power and supply costs for operating Stack II totaled \$0.42 per thousand gallons of product produced. A cost breakdown is shown in table 5.

Electrodialysis

Unit Description and Operation. The electrodialysis unit (ED) was operated in the summers of 1967 and 1968. A more consistent operation was possible in 1968, and this report is concerned primarily with that run. During this period, it was operated on essentially the same blended water (figure 7) as the reverse osmosis unit. The

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
IAWWTC - FIREBAUGH, CALIFORNIA
REVERSE OSMOSIS DATA
TOTAL DISSOLVED SOLIDS VERSUS TIME

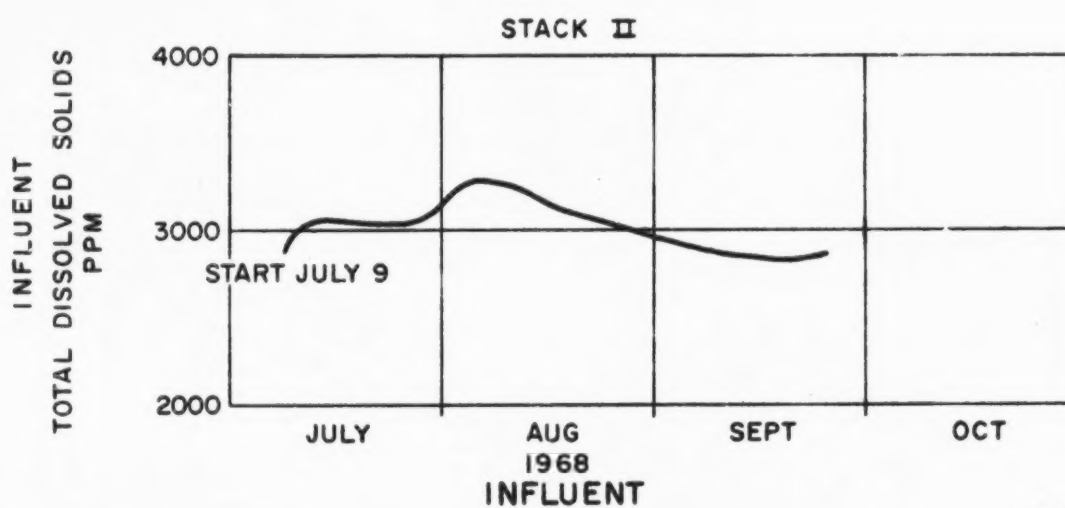


FIGURE 9

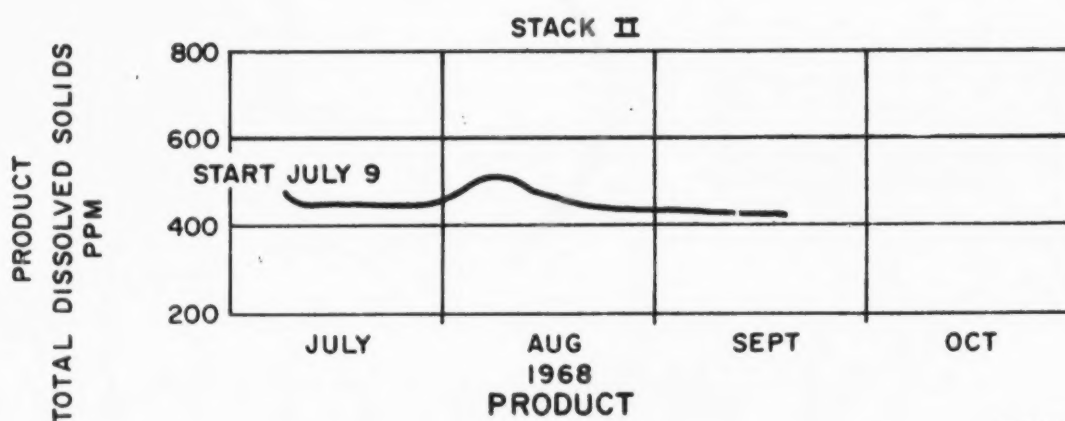


FIGURE 10

FIGURE II

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
IAWQTC - FIREBAUGH, CALIFORNIA
REVERSE OSMOSIS DATA
PRODUCT FLUX VERSUS TIME

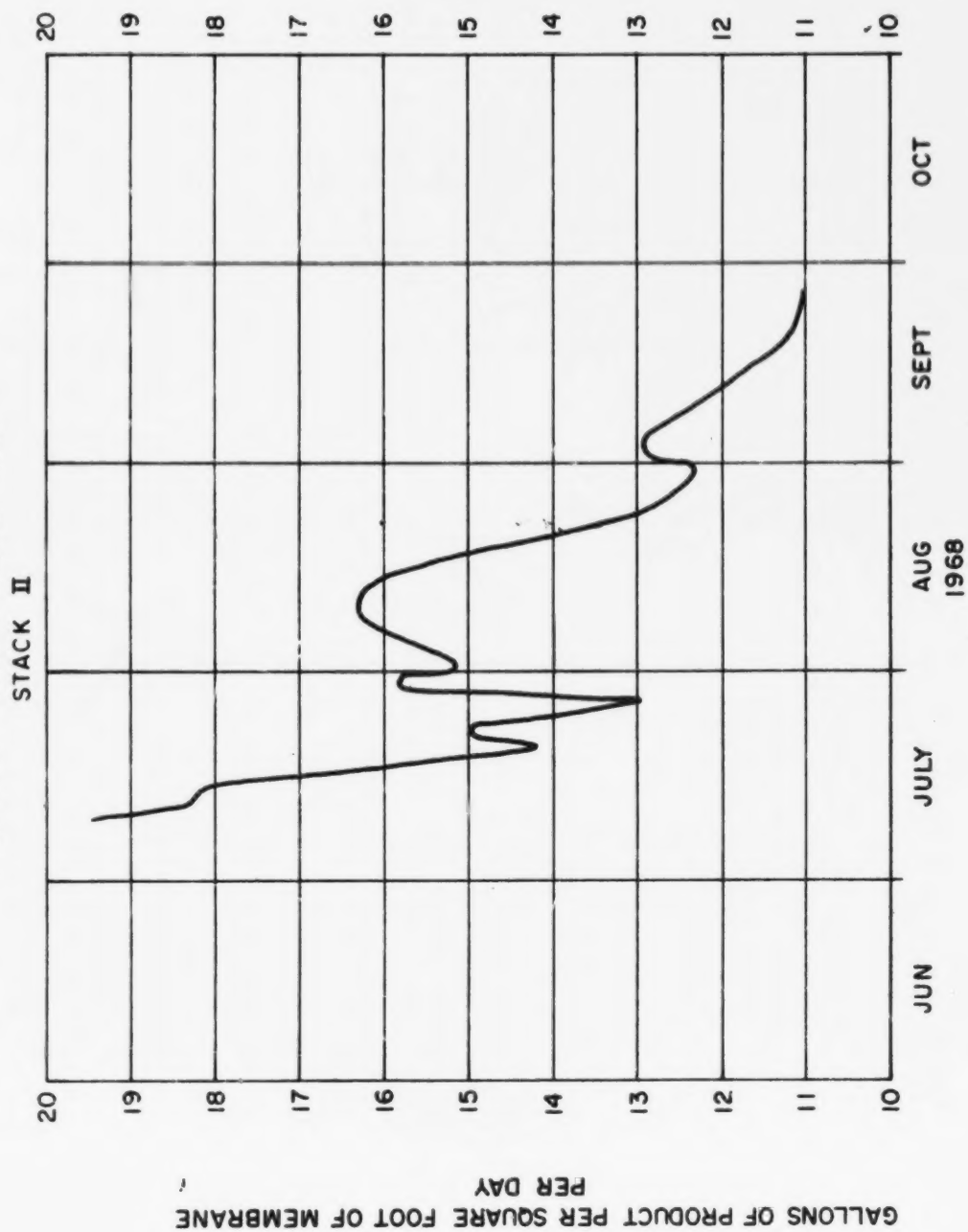


TABLE 4

REVERSE OSMOSIS
Stack II
Mineral Analysis

Operating Conditions

Date of Sample - August 9, 1968
 Operating Pressure, psig - 375
 Temperature of Feed Water - 74°F
 pH of Feed Water - 5.3

Ion	PPM		
	Feed	Product	Brine
Ca ⁺⁺	157	2.5	331
Mg ⁺⁺	85	1.2	161
Na ⁺	665	140	1270
K ⁺	4.3	1.0	7.0
B	7.0	7.0	7.3
SO ₄ ⁼	1650	6.9	3480
HCO ₃ ⁻	55	21	79
Cl ⁻	320	196	400
NO ₃ ⁻	22	24	20
Fe (total)	0.05	0.02	0.04
SiO ₂	30	17	48
Total Alkalinity	46	17	65
Total Hardness	742	11	1490
T.D.S.	2930	381	5900
pH*	6.8	6.8	7.0

* pH at time of sample analysis.

REVERSE OSMOSIS DATA
STACK II

Cost Item	Cost Analysis		Cost Per Million Gallons Product
	Quantity Used Per Million Gallons of Product	Cost	
Sulfuric Acid	2.74 Tons	\$31.60/Ton *	\$86.50
Cyanamer P-35	59 lbs.	\$1.00/lbs.	\$59.00
Filter Cartridges 5-Micron	250	\$0.79/each	\$197.50
Power Requirements Kilowatt-Hours	6700 KWRhrs.	\$0.01/KWRhr.	\$67.00

* Based on Tankcar lots. TOTAL \$410.00 per Million Gallons of Product

TABLE 5

Ionics Electrodialysis Demineralizer Model 300-B-3 has 150 membrane pairs and a product capacity of 25 g.p.m. The waste or brine stream flow rate was varied to inhibit the precipitation of calcium sulfate. The average rate was 8 g.p.m. for the experimental run. Calcium carbonate precipitation was prevented by pH control of the brine stream. A basic flow diagram of the unit is shown in figure 12. An electro motive force (EMF) of 275 volts was applied across the stack; current varied with water temperature, membrane conditions, and influent TDS. The water was passed through the demineralizing stack once, although the unit had the capability of recycling the product water.

Performance. The percent TDS removal and effluent TDS concentrations for the electrodialysis unit are shown in figures 13 and 14. The apparent variations in TDS removal from 36 percent to less than 20 percent were highly dependent on the physical condition of the membranes. In general, any sudden improvement in TDS removal was due to a cleansing of the membranes. Typical substances which frequently accumulated within the stack were precipitated salts, biological slimes, and suspended solids. The general decline in efficiency from early August through September is attributed partially to a 10°C. decline in influent water temperature and partially to a general metal and/or biological fouling of the membranes. Both of the above caused an increase in resistance which lowered the TDS removal capacity of the unit.

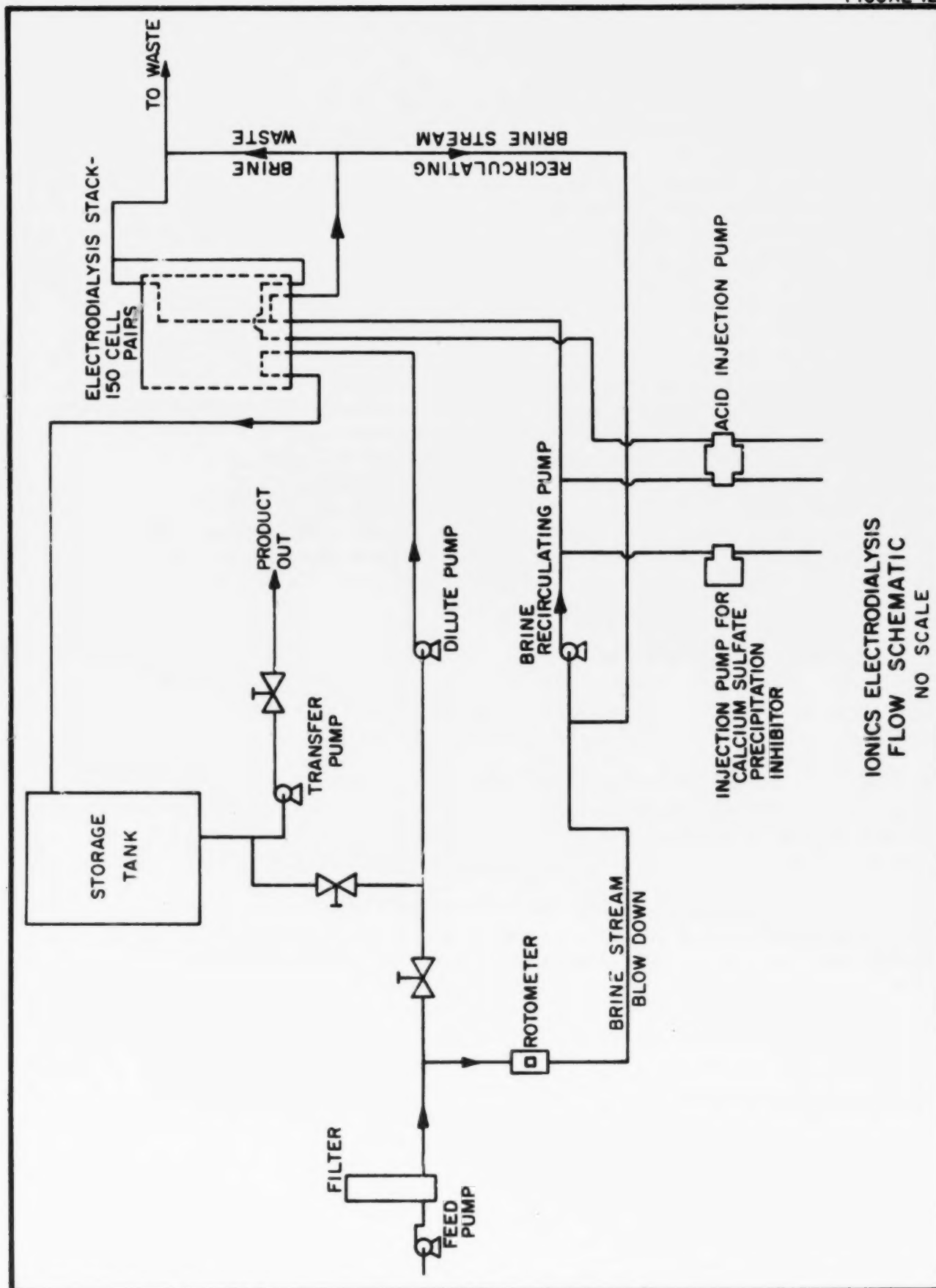
Nitrate was removed with an average rate 1.98 times that calculated for total dissolved solids. This factor compares favorably with the removal range of values reported by Ionics, Incorporated, which was 1.47 to 2.47 times the TDS removal (1)².

No significant boron removal was observed at any time, thus ruling out the use of electrodialysis for reclaiming tile drainage for direct reuse as irrigation water. A summary of common ion removal rates is shown in table 6.

Cost Analysis. The cost for the operation of this unit based on supplies, electrical power consumed, and an average product TDS of 2,300 mg/l was \$0.15 per thousand gallons of water treated. Pro-rating this figure for a multistack unit and a product quality of 500 mg/l TDS, the cost is comparable to the RO unit. Table 7 shows the breakdown of operating costs for the electrodialysis unit.

² Parenthetical numbers refer to literature cited.

FIGURE 12



FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
IAWWTC - FIREBAUGH, CALIFORNIA
ELECTRODIALYSIS DATA
PER CENT REMOVAL OF TDS VERSUS TIME

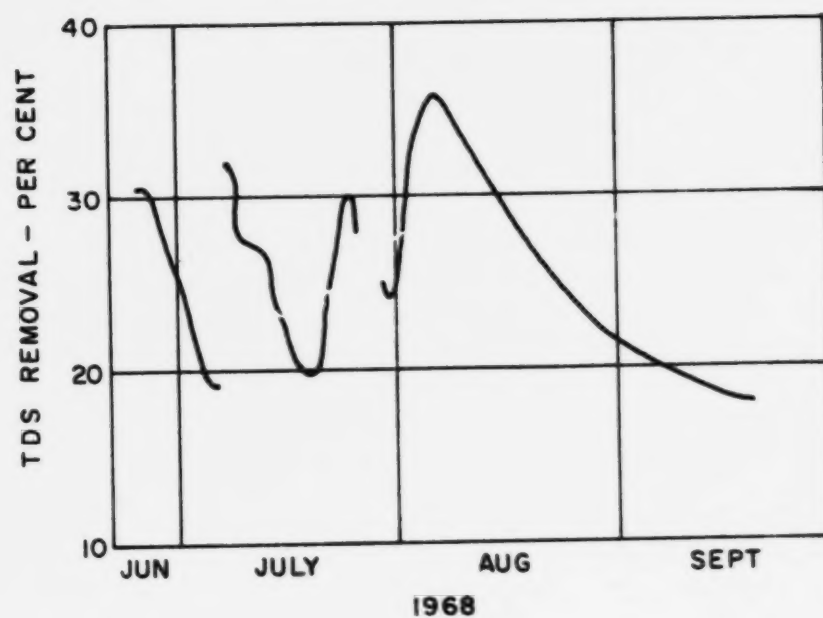


FIGURE 13

TOTAL DISSOLVED SOLIDS VERSUS TIME

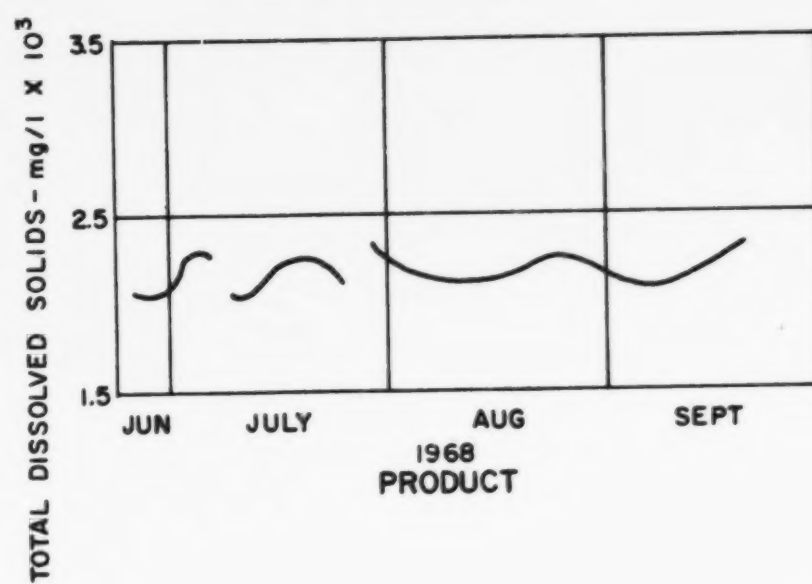


FIGURE 14

TABLE 6

ELECTRODIALYSIS DATA

RUN NO. 1

Date of Sample	July 15, 1968
Brine Stream Dilution--gpm	8
pH of Brine Stream	5.9
TDS Removal-percent	35
Temperature of Influent-°F	75
Applied E.M.F.-volts	276
Stack Current-amperes	13

Ion	PPM		
	Feed	Product	Brine
Ca ⁺⁺	167	105	321
Mg ⁺⁺	68	51	138
Na ⁺	625	515	1060
K ⁺	4.0	2.5	7.6
B	6.7	6.5	6.7
SO ₄ ⁼	1430	1140	2580
HCO ₃ ⁻	336	230	147
Cl ⁻	167	157	593
NO ₃ ⁻	26	14	54
Fe (total)	0.00	0.02	0.02
SiO ₂	29	30	29
Total Hardness	696	473	1370
T.D.S.	3010	2240	5240
pH*	8.1	7.9	7.6

* pH at time of analysis.

TABLE 7

ELECTRODIALYSIS DATA

Cost Analysis

Item	Quantity Used Per Million Gallons of Product	Cost	Cost Per Million Gallons of Product
Sulfuric Acid	1.04 Tons	\$31.60/Ton*	\$32.86
Filter Cartridges	100	\$ 0.79/each	\$79.00
Electrical Power	4250 KWH	\$ 0.01/KWH	\$42.50
TOTAL			\$154.36

*Based on Tankcar lots.

Summary

Desalination of San Joaquin Valley tile drainage water is technically feasible. The initial reverse osmosis stack was able to achieve over 90 percent TDS removal; however, nitrate and boron removals averaged less than 27 percent. The second stack removed 85 percent of the TDS with negligible nitrate and boron removals.

The electrodialysis unit had an average TDS removal of 23 percent with a maximum of 36 percent. The cost for supplies and power for reverse osmosis (Stack II) was \$0.41 per thousand gallons of product. The same costs for electrodialysis came to \$0.15 per thousand gallons of product, with a comparable cost to reverse osmosis for a product of 500 mg/l TDS.

Papers Cited

- (1) Katz, William E., NITRATE REMOVAL BY ELECTRODIALYSIS--A Brief Review, Ionics, Incorporated, October 25, 1966.

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BACTERIAL DENITRIFICATION OF AGRICULTURAL TILE DRAINAGE

By

Thomas A. Tamblyn, Perry L. McCarty,
and Percy P. St. Amant¹

Introduction

Man cannot continue degrading his environment. When he was a nomad he did not have to worry about ecology. If he destroyed one area, all that was necessary was to pick up and move on. As his culture changed, he was no longer able to simply move away from the messes he created, so he began sweeping the problem under the carpet. This process of just covering up the problem has continued to the present time. The country paid little attention to Teddy Roosevelt when he told Congress on December 3, 1907, that:

"To waste, to destroy our natural resources, to skin and exhaust the land instead of using it so as to increase its usefulness, will result in undermining in the days of our children the very prosperity which we ought by right to hand down to them amplified and developed."

However, for some unexplained reason, there is a change taking place. The public is demanding a change in philosophy. This report is an example of what is being done to satisfy this demand. It presents the results of one of the many studies of advanced waste treatment that have been undertaken in the past few years. The objectives of the study were to determine if bacterial denitrification of agricultural tile drainage was feasible under field conditions, and if it was, to develop information on process costs.

Process Considerations

Bacterial denitrification is accomplished by both dissimilatory and assimilatory means. Dissimilatory nitrate reduction is coupled to energy metabolism. The nitrate ion acts as the terminal hydrogen acceptor in the energy transport system. When an adequate concentration of a degradable organic material is present, many facultative bacteria are capable of bringing about dissimilatory nitrate

¹ Sanitary Engineer, Federal Water Pollution Control Administration, Fresno, California; Professor of Environmental Engineering, Stanford University, Stanford, California; and Director, San Joaquin Project, Federal Water Pollution Control Administration, Ada, Oklahoma, respectively.

reduction under anaerobic (or near anaerobic) conditions. Among these are bacteria in the genera; Pseudomonas, Achromobacter, and Bacillus. Assimilatory nitrate reduction is accomplished by reduction of nitrate-nitrogen to the ammonia valence and the subsequent incorporation of the nitrogen into cellular material (1).²

There are differences in the abilities of various bacteria to bring about denitrification (2). Several bacteria can only reduce nitrate to nitrite, while others can only reduce nitrite to molecular nitrogen, while still others are capable of reducing both nitrate and nitrite to molecular nitrogen. In addition, the fraction of the total denitrification process attributable to either dissimilatory or assimilatory reduction varies for different organisms. However, these differences are masked and become insignificant when working with mixed cultures, and the general equation which follows can be formed for the process. McCarty, et al., have presented the development elsewhere and it will not be given in this paper (3).

$$C_m = (1.90 N_o + 1.18 N_1 + 0.67 D_o) C_r \dots \dots \dots (1)$$

C_m = required concentration of degradable organic material, mg/l.
 N_o = nitrate-nitrogen concentration, mg/l.
 N_1 = nitrite-nitrogen concentration, mg/l.
 D_o = dissolved oxygen.
 C_r = consumptive ratio.
 C_r = actual organic carbon sources requirement
 stoichiometric requirement for dissimilatory denitrification and deoxygenation.

The consumptive ratio not only varies between organisms, it also varies with the nature of the organic material being degraded and possibly with the environment in which the degradation is taking place (3), (4). Since tile drainage does not contain a significant concentration of degradable organic material, chemical addition is required for denitrification. Several organic compounds have been screened to determine which compound should be used. Methanol was picked for reasons of economics, a comparatively low consumptive ratio, ease of handling, etc. (5).

Process Configurations

Once it has been determined that a biological process is technically feasible, it is necessary to study possible process physical configurations. These studies must be made to determine which is optimum

² Parenthetical numbers refer to literature cited.

for the problem at hand. There are three basic sanitary engineering process configurations which could possibly be used for bacterial denitrification: anaerobic activated sludge, anaerobic ponds, and anaerobic filters.

Anaerobic activated sludge for the denitrification of municipal waste has been studied under both laboratory and field conditions with and without chemical additions (6, 7). Work is currently underway at several locations to develop design criteria for this configuration (8, 9). The anaerobic activated sludge process was not included as part of the investigation reported on in this paper.

Studies of bacterial denitrification in completely mixed and partially mixed laboratory scale simulated anaerobic ponds have been made (4, 5). Because of the long detention times (several days) required for this process, it has been considered impractical for most situations. However, because of the low cost of construction and the availability of land in the San Joaquin Valley, the decision was made to include anaerobic ponds as part of this investigation.

In the anaerobic filters, the waste is passed through a flooded, packed column-type reactor (a vessel containing an inactive medium). A bacterial mass, that is similar to the zoogloeal film in a trickling filter, develops on the media, allowing the use of short detention times without solids separation and recycle (10). Down-flow anaerobic filters are and have been operated for bacterial denitrification with methanol as the electron donor (11, 12). Upflow anaerobic filters were operated for this investigation in order to avoid duplication of effort and to fill a gap that existed in the available information on anaerobic filters.

Experimental Procedures

The primary objective of this study (to determine if bacterial denitrification of agricultural tile drainage was feasible under field conditions) required that the processes be tested under conditions which duplicated, as nearly as possible, those to be encountered if a full-scale plant were constructed. As a consequence of this, the Interagency Agricultural Waste Water Treatment Center was constructed near Firebaugh, California. It is located in one of the areas of the San Joaquin Valley where there are existing drainage problems (figure 1). The climatic conditions and the quality of available tile drainage (table 1) were nearly ideal for the investigation.

Anaerobic Ponds

The feasibility of bacterial denitrification in deep ponds under field conditions was determined in 3-foot (0.9-m) diameter simulated

FIGURE 1

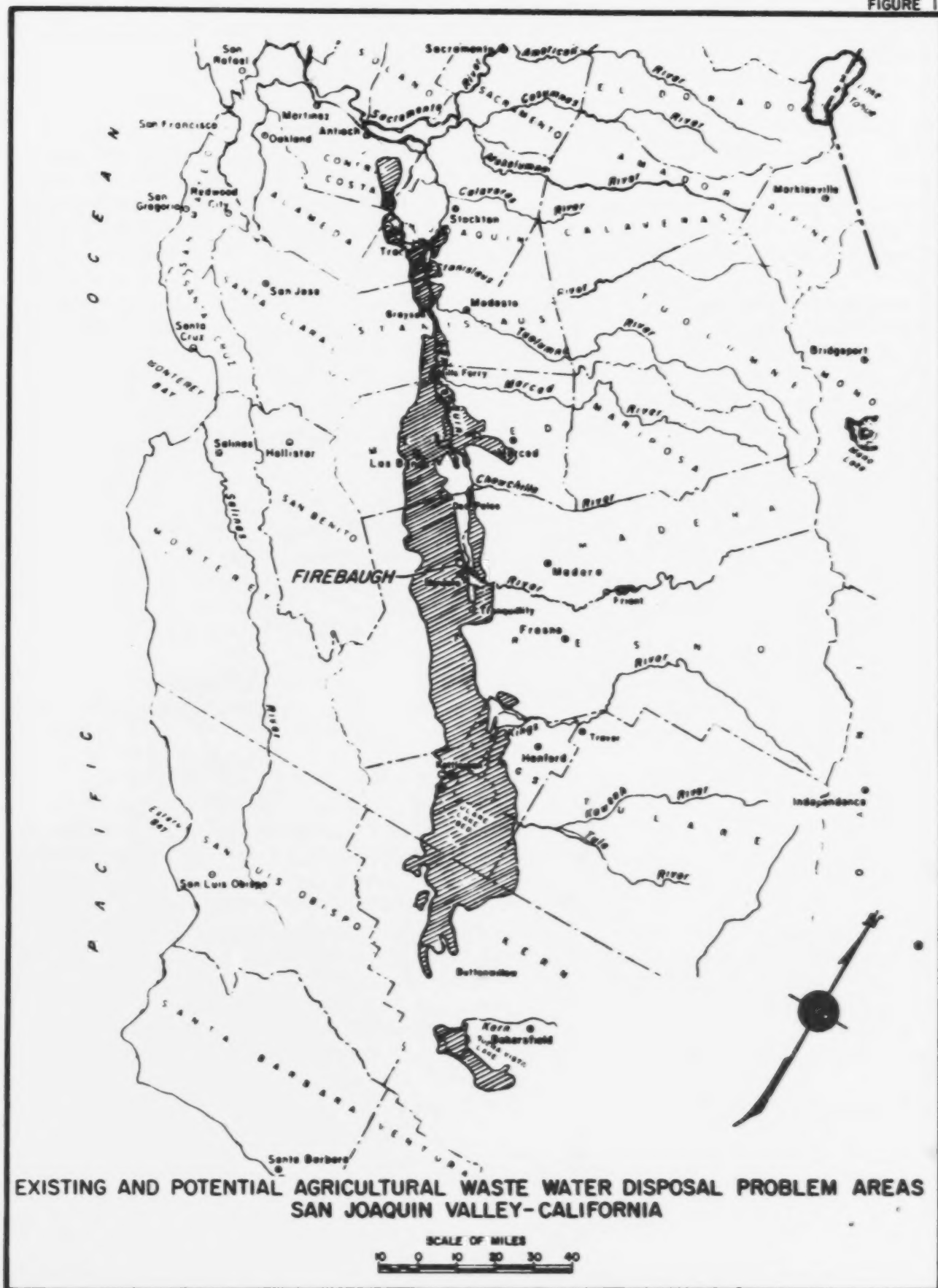


TABLE 1

CHARACTERISTICS OF TILE DRAINAGE USED AT THE INTERAGENCY
AGRICULTURAL WASTE WATER TREATMENT CENTER

Constituent	:	Range of Concentrations mg/l
Total Dissolved Solids	:	2500 - 7600
Salts	:	
Sulfate	:	1500 - 3900
Sodium	:	620 - 2050
Chloride	:	310 - 640
Calcium	:	160 - 390
Magnesium	:	70 - 230
Bicarbonate	:	280 - 330
Potassium	:	4 - 11
Boron	:	4 - 15
Nutrients	:	
Nitrogen	:	5 - 25
Phosphate	:	0.13 - 0.33
Pesticides	:	< 0.001
Others	:	
5-Day BOD	:	1 - 3
COD	:	10 - 20
DO	:	7 - 9

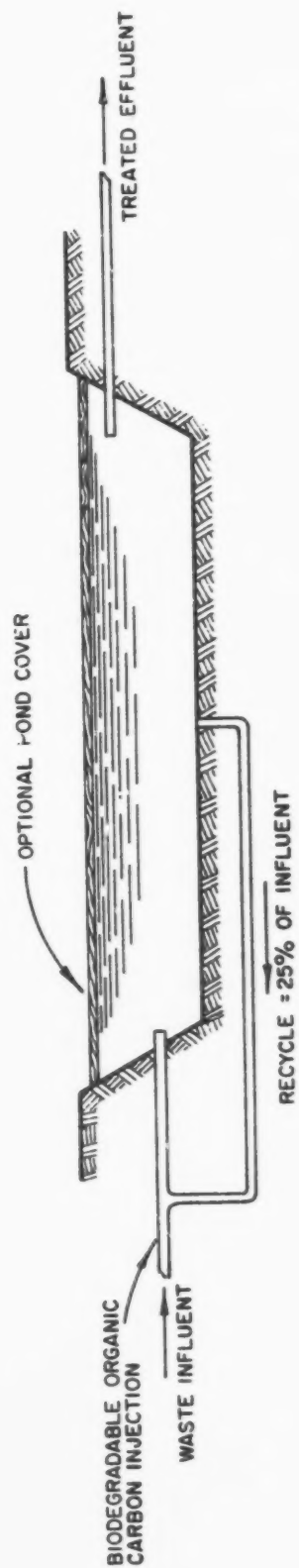
deep ponds (13). Once the process was shown to be feasible, two large ponds were constructed as shown schematically in figure 2. The larger of the two ponds constructed at the Center is 200x50 feet (61 X 15-m) and has a floating cover. The smaller pond is 50x50 feet (15 X 15-m) and is not covered. Both ponds are approximately 15 feet (4.6-m) deep. To increase the solids retention time, recycle is necessary. Through the parallel operation of these two units, it was possible to evaluate the significance of wind mixing and algal growth on process efficiency.

Anaerobic Filters

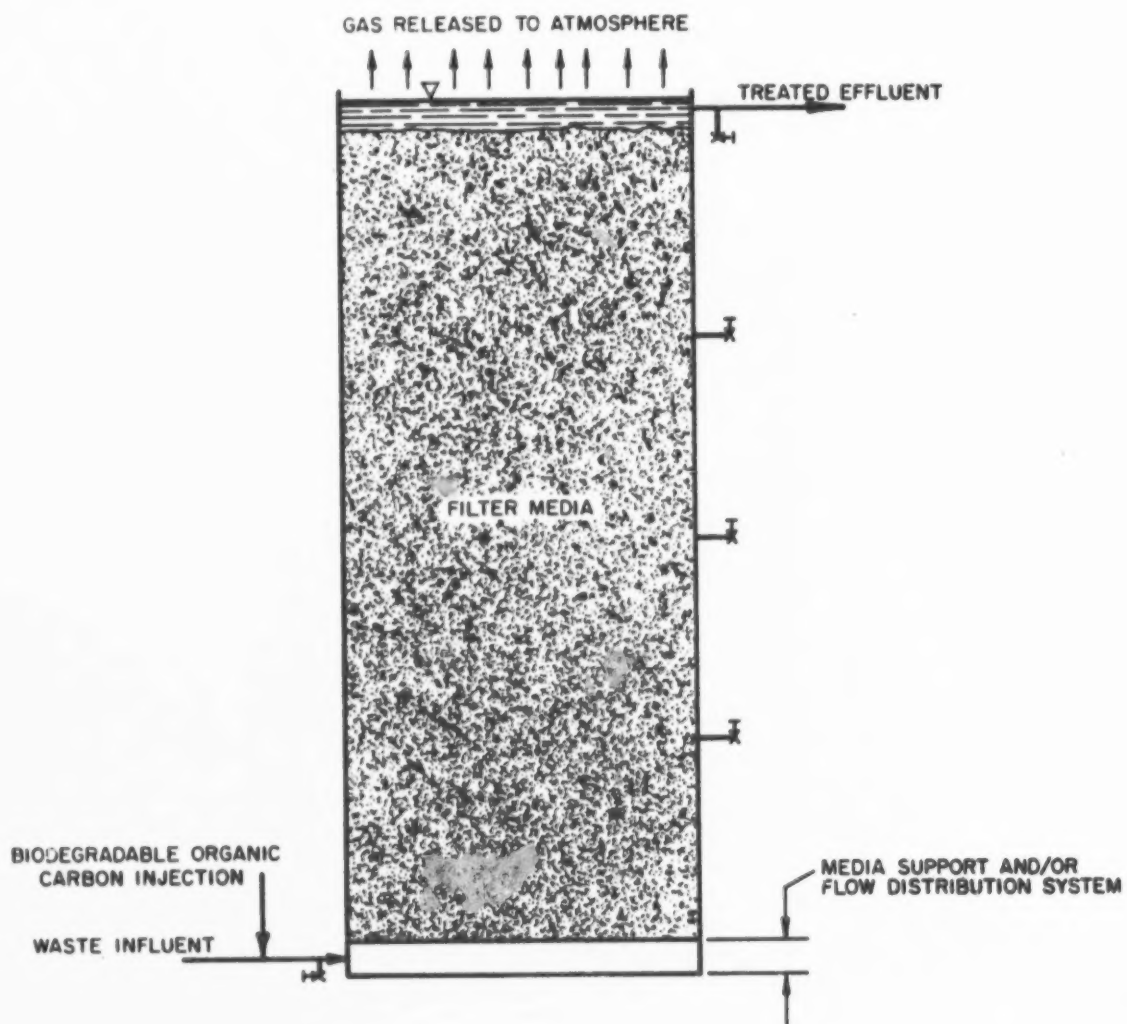
Figure 3 is a schematic diagram of the upflow anaerobic filters used at the Center. Anaerobic filters with 6-foot bed depths which were 4-, 18-, and 36-inch (10-, 46-, and 91-cm) diameter and 10x10 foot (3-m X 3-m) square have been used at the Center (14). The 10x10-foot filter has a false bottom (of the type used in water treatment rapid sand filters) with an 8-inch (20-cm) plenum. The primary purpose for building this filter was to investigate the effect of scale-up on process efficiency due to changes in the hydraulic regime.

Analytical Techniques and Sample Gathering

The routine analyses used to monitor the operation of the various units at the Center are summarized below. Most samples were normally collected between 8:00 and 9:00 a.m., and analyzed immediately. Some samples were taken in the afternoon to gather information on changes that may have occurred during the peak photosynthetic period. Diurnal studies were also conducted, as the need arose.



SCHEMATIC DIAGRAM
DEEP POND DENITRIFICATION PROCESS



LEGEND
 T OPTIONAL SAMPLE TAPS

SCHEMATIC DIAGRAM
 UPFLOW ANAEROBIC FILTER DENITRIFICATION PROCESS

ROUTINE ANALYSES PERFORMED AT THE
INTERAGENCY AGRICULTURAL WASTE WATER TREATMENT CENTER

<u>Analysis</u>	<u>Technique</u>
Nitrate-Nitrogen	Brucine Method and/or Selective Ion Electrode
Nitrite-Nitrogen	Standard Methods, 12th Edition (15)
Total Kjeldahl Nitrogen	Kjeldahl Method
Ammonia Nitrogen	Distillation Method
Organic Nitrogen	Kjeldahl Method
Orthophosphate	Stannous Chloride Modification
pH	Glass Electrode
Alkalinity	Standard Methods, 12th Edition
Dissolved Oxygen	Winkler Method
Suspended Solids	0.45 u Glass Paper, 103°C.
Volatile Suspended Solids	0.45 u Glass Paper, 600°C.
Optical Density	450 u, 5 cm Cell
Electrical Conductivity	Galvanic Cell
Algal Cell Counts and Identifiers	Sedgewick-Rafter Cell
Methanol	Gas Chromatograph, Carbowax Column, Flame Ionization Detector

In addition to chemical analyses, several physical parameters were monitored. Water temperatures were monitored daily with maximum-minimum thermometers and periodically with 8-day recording thermographs. The influent pressure required for an anaerobic filter to maintain a constant hydraulic detention time was monitored with varying frequency throughout the study. Flows were calibrated volumetrically. In addition, tracer studies using the chloride ion as a tracer were run to determine the actual hydraulic regime of the different units. Pre- and post-injection density corrections were made using sodium sulfate. The tracer studies were analyzed using the volume apportionment technique (16).

Results and Discussion

The initial field studies of bacterial denitrification in simulated deep ponds indicated that significant denitrification could take place in ponds with detention times as low as 5 days (13).

Data gathered from the large ponds, which started operation in the fall of 1968, are summarized in table 2. The covered pond has consistently outperformed the uncovered one. There are two primary reasons for this. Large algal populations develop in uncovered ponds and the resultant high dissolved oxygen concentration inhibits

TABLE 2
DEEP POND DENITRIFICATION
NITROGEN REMOVAL-DETENTION RELATIONSHIP

Detention Time Days	Number of Days of Operation		Nitrogen Removal in Percent					
	Uncovered Pond	Covered Pond	Uncovered Pond		Covered Pond			
			Min.	Max.	Avg.	Min.	Max.	Avg.
7.5	-	34	-	-	-	67	92	80
10	61	31	60	93	77	75	98	88
15	30	35	30	95	56	88	94	91
20	31	40	54	84	71	84	94	90

denitrification. The second reason is that more of the influent is short-circuited through the uncovered pond because of wind mixing and temperature variations. The high nitrogen removal efficiencies recorded for the uncovered pond, when operated with a 10-day detention time, was probably caused by the formation of a natural partial cover. The cover was composed of decayed algal and bacterial cells floating on the surface of the pond. Some type of covering is necessary for sufficient denitrification to take place. Research is currently underway to determine if a floating vegetative mat may be used in place of fabricated pond covers. There have been numerous mechanical equipment breakdowns associated with these units; therefore, it is, as yet, impossible to accurately predict the minimum detention time possible. However, a 10-day detention time with 25 percent recycle and a pond depth of 15 feet have been shown to be effective for covered pond summertime operation (table 2) and these criteria were used for developing process costs.

The data from experiments designed to investigate the significance of anaerobic filter media size, texture, and sorptive quality are summarized below (14).

NITROGEN REMOVAL EFFICIENCIES FOR
FILTER DENITRIFICATION UNITS CONTAINING VARIOUS MEDIA

<u>Medium</u>	<u>Nitrogen Removal Efficiency, Percent</u>		
	<u>Min.</u>	<u>Max.</u>	<u>Average</u>
Activated Carbon	89	99	96
Washed Sand	84	97	93
5/16" Coal	80	98	93
5/16" Volcanic Cinders	85	98	94
3/8" Aggregate	82	97	94
5/8" Volcanic Cinders	87	97	91
1" Coal	81	98	93
1" Volcanic Cinders	89	97	96
1" Aggregate	89	98	94

Based on the results of an initial feasibility investigation, all filters operated to generate this data had hydraulic detention times (based on void volumes) of 2 hours. Medium surface texture, size, and sorptive quality had no apparent effect on removal efficiencies. After an extended period of continuous operation, the bacterial mass within filters containing media with diameters of less than 1 inch built up to the point where the required influent pressures (as high as 60 p.s.i.g.) rendered them uneconomical.

The data gathered from the long-term operation of three filters containing 1-inch-diameter media are summarized in the following table:

SUMMARY OF LONG-TERM PERFORMANCE
OF FILTERS CONTAINING ONE-INCH-DIAMETER AGGREGATE

Detention Time Hrs.	Days of Operation	Percent Nitrogen Removal			Required Influent Pressure, psig		
		Min.	Max.	Average	Min.	Max.	Average
0.5	275	40	91	68	3.5	11.8	7.2
1.0	240	64	97	88	3.2	9.6	5.4
2.0	244	79	97	91	3.5	9.7	6.2

For about the first 150 days of operation, the required influent pressure fluctuated within a narrow range. There did not appear to be any need for backwashing, etc. Since that time, an upward trend has begun to appear. Investigations are currently underway to determine the best technique for reducing this pressure.

The temperature of the influent to the units varied from a high of 22° to a low of 10° Centigrade. There were some indications of a relationship between temperature and nitrogen removal efficiency. The units that were run with 0.5- and 1-hour detention were less efficient during the colder part of the year than during the summer months. This phenomenon did not hold true for the unit operating at 2 hours. As the temperature of its influent dropped, the length of the filter bed required for treatment increased. The 6-foot bed depths used for this investigation and the range of temperatures encountered were such that the effect was not reflected in the overall treatment efficiencies of the unit. Process costs for anaerobic filters were developed assuming a summer detention time of 1-hour with a 6-foot bed of 1-inch-diameter aggregate.

The average consumptive ratio calculated from the data gathered at the Center equals 1.47 mg/l with a standard deviation of ± 0.367 . The large standard deviation calculated for the consumptive ratio is more likely due to inherent difficulties in field studies than to fluctuations in system requirements. No difference could be seen between pond and filter methanol requirements. With the development of an automatic methanol control system, which would respond to changes in influent and effluent quality, this variation should be drastically reduced. The methanol requirement for a typical influent containing 20 mg/l of nitrate-nitrogen and 8 mg/l of dissolved oxygen calculated by equation (1) equals 64 mg/l.

As mentioned above, process costs have been estimated using the operating criteria necessary during the warmer season of the year. Computer simulation and an extensive water quality monitoring program have yielded predictions of the seasonal variations that will occur in the flow rate and nitrogen content of the waste requiring treatment (17, 18). These predictions show that 70 percent of the annual nitrogen load, in pounds per day, will arrive at the treatment plant between April 1 and September 30 (the warmer season). A bacterial denitrification plant designed to treat this load will have more than adequate capacity for winter operation.

The estimated costs that have been made to date (December 1969) indicate that treatment in either anaerobic ponds or filters will most likely cost between \$30 and \$60 per million gallons of waste treated. Plant designs for various influent rates are presently being made. They will be used to develop equations for the relationship of plant design capacity to costs per million gallons of waste treated. From a comparison of the estimated range of treatment costs and the conclusions of the Bay-Delta Report (19), it can be said that agricultural tile drainage can be treated and discharged to the San Francisco Bay System at less cost than that of any alternative plan.

Conclusion

It has been shown that bacterial denitrification in covered anaerobic ponds and anaerobic filters are both feasible under field conditions. Additional work is needed on the actual costs of treatment using the processes. However, preliminary estimates indicate that agricultural tile drainage can be treated at a cost that is substantially below the economic constraint that has been placed on the system.

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ALGAL NUTRIENT RESPONSES IN AGRICULTURAL WASTE WATER

By

James F. Arthur, Randall L. Brown,
Bruce A. Butterfield, and Joel C. Goldman¹

Introduction

In 1960, the Congress of the United States authorized the Bureau of Reclamation, under Public Law 86-488, to construct a drainage disposal facility for the Federal San Luis Service Area in the Central San Joaquin Valley of California. That same year, the California State Legislature, with voter ratification, passed the California Water Resources Bond Act, which included a study of agricultural waste-water drainage facilities in California.

The necessity for such legislation has arisen because of the increasing demand for westside farmland, which though very rich in nutrients, requires salt leaching to maintain a salt balance. Unfortunately, the southern portion of the San Joaquin Valley is almost a closed basin in which there is no natural drainage available for removal of this waste water. Thus, the California Department of Water Resources has estimated that by the year 2020, the annual amount of brackish agricultural waste water requiring disposal will be about 580,000 acre-feet per year.

The San Joaquin Valley Drainage Investigation (Lindholm, 1965), which was initiated as a result of the 1960 enactment, concluded that of several waste-water disposal plans proposed, three were most likely to prove practical; namely, desalinization, evaporation, or transportation (removal) of the water from the valley. Further investigation indicated that the latter method would probably be the most economical, and that if this method were selected for disposal, the most convenient transportation route would be by way of a drain running up the Central Valley through the Delta-San Francisco Bay System and into the ocean. Unfortunately, this method of disposal would mean discharging nitrogen into a water system already heavily taxed with domestic and industrial waste (Beck and St. Amant, 1968; Stetson and Price, 1968). To find ways of solving the potential pollution problems that could arise in the Bay, the Interagency Agricultural Waste Water Treatment Center (IAWWTC) at Firebaugh, California, was established by a joint task force consisting of the

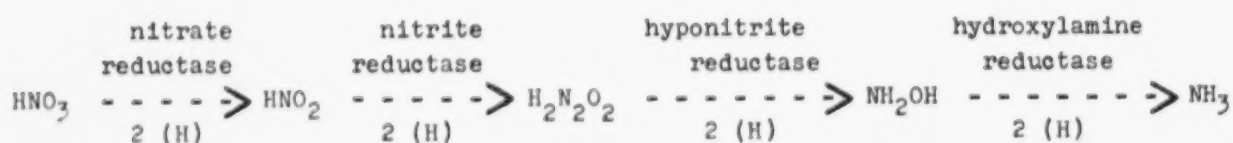
¹ Research Aquatic Biologist, Federal Water Pollution Control Administration; Associate Water Quality Biologist, and Assistant Civil Engineers, California Department of Water Resources, respectively; Fresno, California.

Bureau of Reclamation (USBR), the California Department of Water Resources (DWR), and the Federal Water Pollution Control Administration (FWPCA), to study the economic and practical feasibility of biologically removing nitrate-nitrogen from agricultural waste water (Beck, Oswald, and Goldman, 1969).

After 1-1/2 years of actual pre-pilot operation, two biological removal processes, anaerobic bacterial denitrification and algal nutrient stripping, show the most promise as practical methods of removing nitrate from eutrophicated waters (Beck and St. Amant, 1968; Beck, Oswald, and Goldman, 1969; St. Amant and McCarty, 1969; Tamblyn and Sword, 1969). The algal stripping process is the subject of this paper.

The theory behind the algae stripping method of nitrogen removal is simple; namely, any nutrient (e.g. nitrogen) required by algae can be removed from the growth medium by assimilation and subsequent conversion to cellular material. The algae, along with the incorporated nutrient, can then be removed from the medium. Theoretically, maximum nutrient assimilation by algae will occur if the nutrient to be removed is the one limiting factor; however, in actual practice this is often difficult to obtain.

In general, all algae can utilize inorganic nitrogen as either ammonium salts or nitrates. The reduction process by which inorganic nitrogen is utilized requires energy in the form of light and is temperature dependent. The basic reaction by which nitrates are reduced to ammonia generally is thought to occur in four stages as follows:



The end product, ammonia, is then transferred to the amino acid pool where it can be utilized in the formation of protein. The products of nitrogen assimilation, which have been determined in Scenedesmus, the species studied at the IAWWTC, indicate an immediate increase in cellular, soluble organic-N; followed by an increase in insoluble-N, if sufficient carbohydrate is available (Lewin, 1967).

In addition to seasonal changes in physical factors such as light and temperature, changes may occur in the nature and concentration of nutrient constituents in the growth medium. These nutrient changes may limit physiological responses and mask the effects of other environmental parameters. One such nutrient is phosphorus. It is

one of the major nutrients required for normal algal growth and normally comprises about 1 percent of the organic material of algae. Changes in its availability can be brought about by shifts in pH level, which leads to altering of the rate of phosphate uptake from the medium, either by a direct effect on permeability of the cell membrane, or by changing the ionic form of the phosphate, which in turn can limit nitrate uptake. The latter effect of pH on phosphate uptake appears to be the case at the IAWWTC, where high alkalinity levels (300-400 mg/l CaCO_3) along with increased pH (due to algal assimilation of carbon as CO_2) results in the precipitation of phosphate salts. In addition, a reserve of available carbohydrates, which is dependent upon carbon availability, also plays an important role in phosphate uptake, since carbohydrate degradation by oxidative phosphorylation is needed to provide energy for the uptake process. Accordingly, when phosphate is deficient in the growth medium, there is an accumulation of cellular fat, starch, and wall substance, indicating an interference with nitrogen metabolism (Lewin, 1967). Fluctuation in the amount of available phosphorus can, thereby, affect algal growth and nitrate assimilation altering the effect of other parameters being measured.

The availability of trace elements also affects growth and nitrogen assimilation (Fogg, 1965). For example, as molybdenum becomes deficient in the medium, the growth rate decreases. A lack of iron, another essential trace element, leads to a decrease in chlorophyll level which, in turn, limits the cells' photosynthetic activity and, thence, its growth. Furthermore, iron (as well as other metals required for growth) is only slightly soluble in well oxygenated and/or basic water (Ruttner, 1965), and the availability of such nutrients to algae in the precipitated form is dubious. Unfortunately, these are the conditions typically found in high rate algal ponds, since algae both produce oxygen and use CO_2 in the photosynthetic process. This utilization of CO_2 by actively growing algae usually reached a point at which the CO_2 level in the growth medium is not in equilibrium with the atmosphere, and the pH of the medium, therefore, will rise. The pH increase, in turn, affects the solubility and, hence, the availability of other nutrients. A slowdown of growth results and, thus, the algae in effect limit their own growth rate. The examples given in this and in the preceding paragraph are but a few of those which can be cited on how different nutrient levels can affect algal growth.

The objectives of the IAWWTC are to develop an algal nutrient removal system that is efficient, dependable, and economical. To accomplish these goals, we are attempting to: (a) maximize algal nitrogen assimilation by determining those factors, chemical and physical, which can be rate-limiting, and (b) determine how to compensate for fluctuations in those factors. Preliminary studies had indicated

that detention time, depth, and mixing velocities would probably be the most important parameters affecting the system. However, after several months of operation, it became apparent that some other variable was limiting nitrogen assimilation by the algae in the outdoor growth units. As a result, it was decided to use light box studies to define optimum algal growth and nitrogen assimilation parameters before applying them to the outdoor growth units. This paper presents some of the techniques and results obtained thus far in the light box and outdoor growth studies.

Methods and Materials

Growth Media. Algal growth studies at the IAWWTC are conducted with the use of cultures grown indoors in light boxes and in large outdoor growth units in which agricultural tile drainage water serves as the basic growth medium (Lindholm, 1965). The chemical constituents of this water, which is relatively high in total dissolved solids (TDS), varies seasonally depending upon the irrigation and fertilization practices for the particular crop grown.

Nutrient additives used in the light box studies were of analytical grade. Nitrate-nitrogen (NaNO_3) was added, when required, to the test water to maintain a minimal nitrate-nitrogen concentration of 20.0 mg/l. This concentration is the average predicted for the San Luis Drainage Area. Carbon additions were made by the injection of atmospheric air, bottled 4 percent, or 100 percent CO_2 (passed through a water scrubber) directly into the flasks; or in the case of the outdoor growth units, into the intake side of the mixing pumps.

Growth Unit - Light Box. The light box at Firebaugh consists of two shelves, 12x3 feet with lighting provided by eight 6-foot, cool-white, fluorescent lamps placed 15 inches above the surface of each shelf. Light intensities at the shelf level were approximately 350-400 foot-c. All ballasts were removed from the light fixtures and placed several feet from the light box to minimize temperature increases. The studies were conducted with the use of continuous light (Joint Industry/Government Task Force on Eutrophication, 1969).

Compressed air or bottled CO_2 enriched air was passed through a water scrubber for humidification, i.e., to reduce evaporation loss in the culture containers. The various gas mixtures were distributed to the flasks through a central manifold system. The gas pressure to each flask was equalized by placing a short capillary tube in the air line between the manifold and the flasks.

Although temperature was not controlled to the desired degree ($23 \pm 1^\circ\text{C}$), it remained within the $23 \pm 5^\circ\text{C}$ range. The lack of precise control did not appear to have any adverse effect on the algae.

The use of 500 ml aliquots of medium contained in one-liter Erlenmeyer flasks was found to give maximum growth rates under the experimental conditions used at the Agricultural Waste Water Treatment Center (Brown and Arthur, 1969). Apparently, the resulting surface to volume ratio allowed optimum CO₂ exchange. Cultures of this volume also permitted adequate subsampling for chemical and biological analysis.

Outdoor Growth Units. Twenty 8x16x1.2-foot rectangular plywood fibreglassed units, each having approximately 3,500 l capacity, were used for the outdoor growth studies. Two additional units were used for depth studies, one 18 inches deep and the other 10 inches deep. Detention time in all units was controlled by adjusting the flow through rotometers and were calculated using influent flow rates and pond volumes, not actual hydraulic flows within the units. Mixing schedules were varied by the use of timers on each of the mixing pumps.

In addition to the above growth facilities, the Center has one large (1/4-acre) unit, 200x50 feet, capable of operating at water depths of from 8 to 36 inches. As with the smaller outdoor units, detention time and mixing cycles can be varied.

Inoculum. The predominant algal species used as a test organism at the Agricultural Waste Water Treatment Center has been the green algae, Scenedesmus quadricauda, which was originally obtained from the high-rate algal pond at the University of California's Richmond Field Station, Richmond, California. This particular species was chosen because: (a) it has a known high nitrate requirement, (b) it was available in large quantities, (c) it was relatively easy to separate, (d) it has been successfully used as a food supplement, and (e) it occurs naturally in drainage canals near the IAWWTC, although in relatively low numbers.

Inoculums of Scenedesmus quadricauda used in the light box nutrient bioassay studies usually were from cultures in the log phase of growth grown in the outdoor units. The cell density of the inoculated sample was kept at about 2,000 cells/ml to minimize carryover of nutrients. Although the cultures were neither axenic or even unialgal, they were predominant (95-100 percent) Scenedesmus and were acclimatized to the conditions prevailing at the particular time of the year.

Analyses. Routine analyses of the growth medium used in the light box and the outdoor growth units included analyses for nitrate, nitrite, organic nitrogen, orthophosphate, alkalinity, and pH (American Public Health Association, 1965). In addition, when specifically required, other chemical determinations were made (e.g., iron

determinations, hardness, dissolved oxygen, general trace elements, etc.).

Many of the conclusions reached in the present study were based on nitrate uptake by the algae. Daily or semidaily nitrate-nitrogen analysis was made with a specific ion electrode with random brucine analyses used to establish a daily standard curve. Numerous comparisons of the electrode with the standard brucine method of nitrate determination indicated that this method was much faster than the brucine and subject to smaller variations.

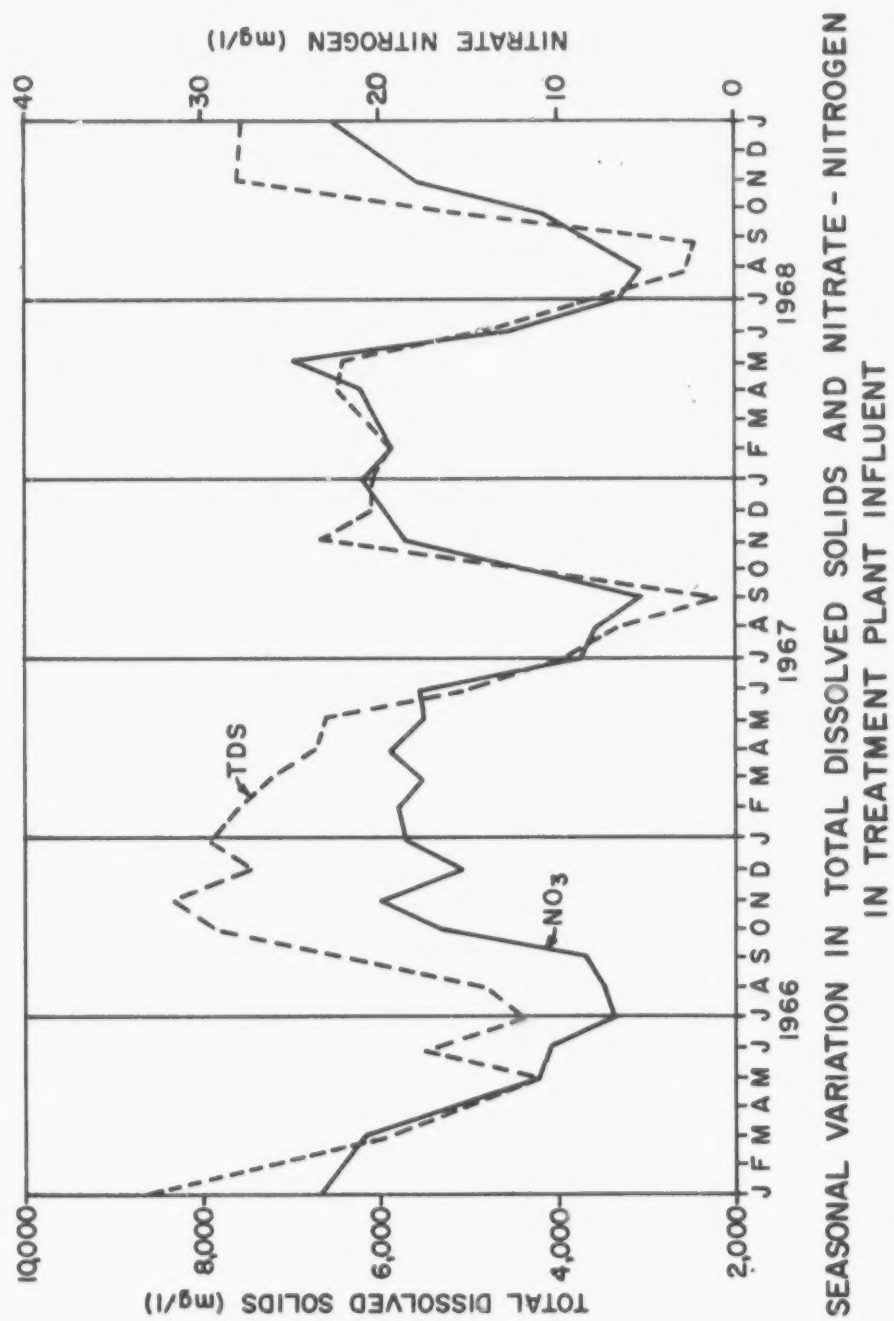
Routine analysis of light box samples included suspended and volatile solids, temperature, absorbence (on a spectrophotometer at 410 mμ), cell counts, and algal species determinations. In addition to the above, total light energy, electrical conductivity, TDS, air and water temperature, wind and precipitation were recorded for the outdoor growth units. As required, measurements were made of other factors affecting the operation of algal growth units.

General Procedure. In order to eliminate as many variables as possible, a covered storage pond having an 820,000-gallon capacity was used to provide a constant supply of water for use in the light box and outdoor growth studies. This large reserve of water allowed a study period of from 60 to 90 days, without significant changes in influent quality, as well as making nutrient additions much simpler. Because of the large fluctuations in nutrient levels between studies (figure 1) an algal nutrient bioassay was conducted in the light box each time the storage pond was filled to determine the optimum nutrient level required for maximum growth rate and nitrogen assimilation. This was normally accomplished by adding varying levels of different nutrients to the tile drainage in a factorially designed experiment (e.g., five levels of iron vs. five levels of phosphorus). A plot of daily nitrate removal from the medium was then used to determine the effect of the various nutrient additions on nitrate assimilation. The optimum level of a particular nutrient or nutrients was then tested to determine if the nitrogen uptake rate could further be enhanced with the addition of other nutrients. These tests usually were conducted at three CO₂ levels (swirled twice per day, air, and 4 percent CO₂). If a particular nutrient was found to be limiting nitrogen assimilation, it was added either to the covered storage pond or to individual growth units.

Results and Discussion

The IAWWTC Site was chosen because: (a) the land was available through the U.S. Bureau of Reclamation, (b) the tile drainage sump had a large flow volume, and (c) the water had an average nitrogen level which was close to the predicted average value for the drainage

FIGURE 1



area. In table 1 are shown the average predicted monthly flows, nitrates, phosphates, and total dissolved solids expected in the San Joaquin Valley agricultural waste-water drain. Note that the predicted average nitrate-nitrogen concentration will be about 20 mg/l.

Because of irrigation practices in the area of the IAWWTC over the last 3 years, the major nutrient constituents have varied considerably more, see figure 1, than is expected in the overall drain, which draws from a large and varied service area. As a result, certain algal growth characteristics were affected by nutrient variation, inasmuch as the storage pond was filled during different times of the year.

To account for changes in growth patterns resulting from these changes in water quality, we have been conducting routine algal nutrient bioassays (in the light box) on our supply water to determine if any nutrient other than nitrogen is rate-limiting. Unfortunately, the results of these studies have not always been applicable to the outdoor growth units. For instance, in the light box cultures there is a very definite year-round 2-4 mg/l phosphate requirement, as well as a 2-4 mg/l iron requirement for part of the year. Figure 2 illustrates the typical relationship between iron and phosphate additions on algal nitrate assimilation, as determined in the light box cultures. Accordingly, during one 30-day study in the outdoor growth units, iron was added to a series of ponds at different detention times. Ponds receiving iron had total nitrogen removal efficiencies 20 percent to 30 percent higher than did the ponds with no iron additions (figure 3a). However, at other times of the year, the addition of iron had little or no effect on nitrogen removal (figure 3b), even though it did show up as rate-limiting under light box conditions.

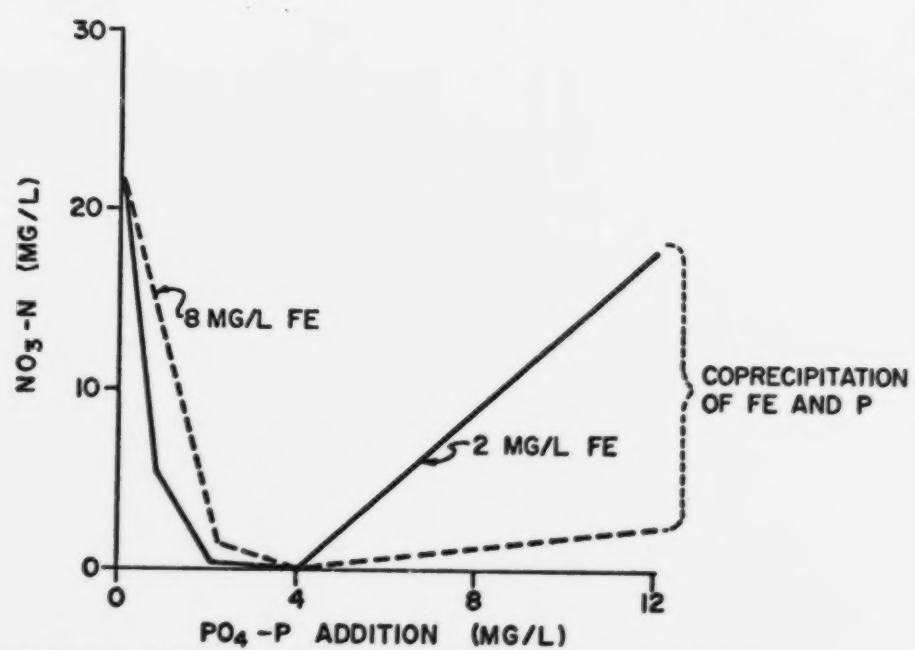
The same inconsistencies in response have been noted with phosphorus. The addition of phosphate to the outdoor growth units (figure 4), though not as well defined as in the light box cultures (figure 2), clearly demonstrates a need for additional phosphate. During certain times of the year, particularly in late spring and early summer when algal growth rates are maximum (optimum light and temperature), the pH level is increased to as high as pH 10 and a noticeable precipitation of phosphate salts occurs. In addition, if the level of either iron or phosphate is increased over the optimum level of both combined, the level of the other must also be increased. This is probably the result of co-precipitation at the normal pH (8-10) and temperature (20-30°C) ranges of the studies (figure 2).

Temperature also has a significant influence on algal nutrient response. As ambient temperatures decrease, algal growth rates also decrease to a level where nutrients are not likely to be limiting

TABLE 1
PREDICTED AVERAGE FLOWS AND NUTRIENT LEVELS
FOR THE SAN JOAQUIN VALLEY AGRICULTURAL WASTE WATER DRAIN

Variable	1967-1968 Average Values												
	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Annual
Flow (Acre-Feet Per Acre)	.052	.064	.082	.093	.149	.170	.195	.184	.128	.075	.054	.053	1.300
Nitrate-Nitrogen (mg/l)	31.9	33.5	33.9	28.0	19.2	17.1	15.4	13.8	15.2	19.5	21.4	23.2	19.8
Phosphate-Phosphorus (mg/l)	.21	.15	.16	.18	.12	.10	.09	.11	.14	.14	.12	.11	.13
Total Dissolved Solids	3434	3623	3737	3764	3388	3152	3119	2758	3065	3210	3194	3249	3215

FIGURE 2



AVERAGE NO₃-N CONCENTRATIONS AFTER 12 DAYS
WITH VARIOUS PO₄-P LEVELS AT TWO FE LEVELS

THE EFFECT OF IRON AND PHOSPHATE ADDITIONS ON NITRATE
ASSIMILATION IN THE LIGHT BOX

FIGURE 3

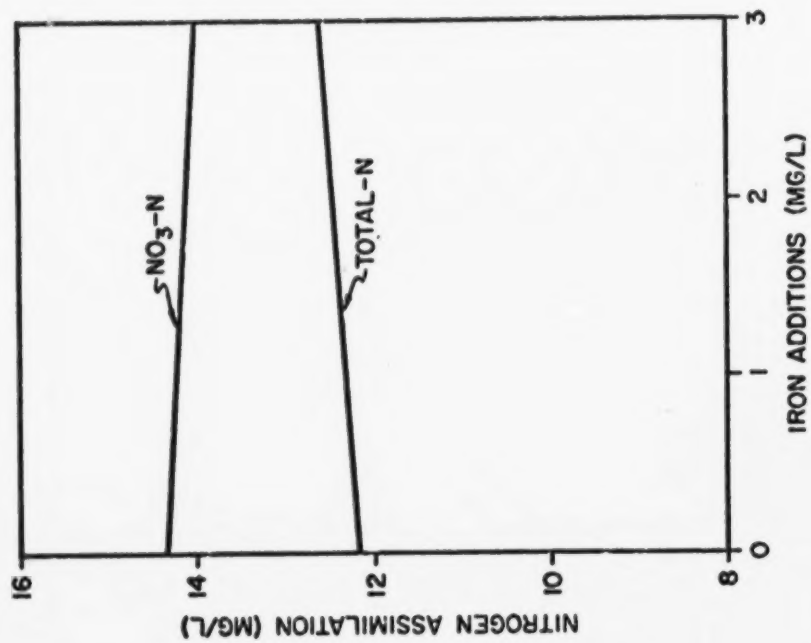


Figure 3-B. EFFECT OF FE ADDITIONS ON
ALGAL NITROGEN ASSIMILATION
IN OUTDOOR GROWTH UNITS IN LATE SUMMER

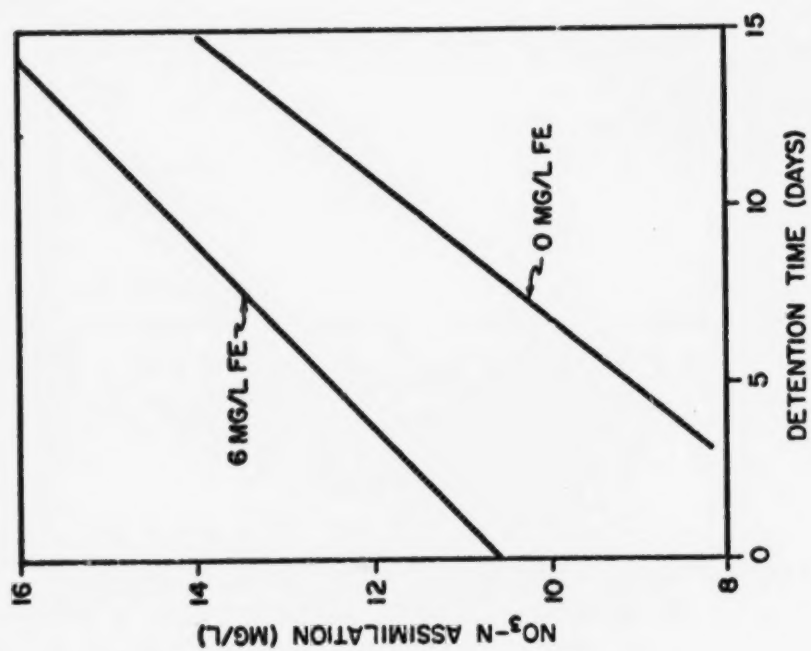
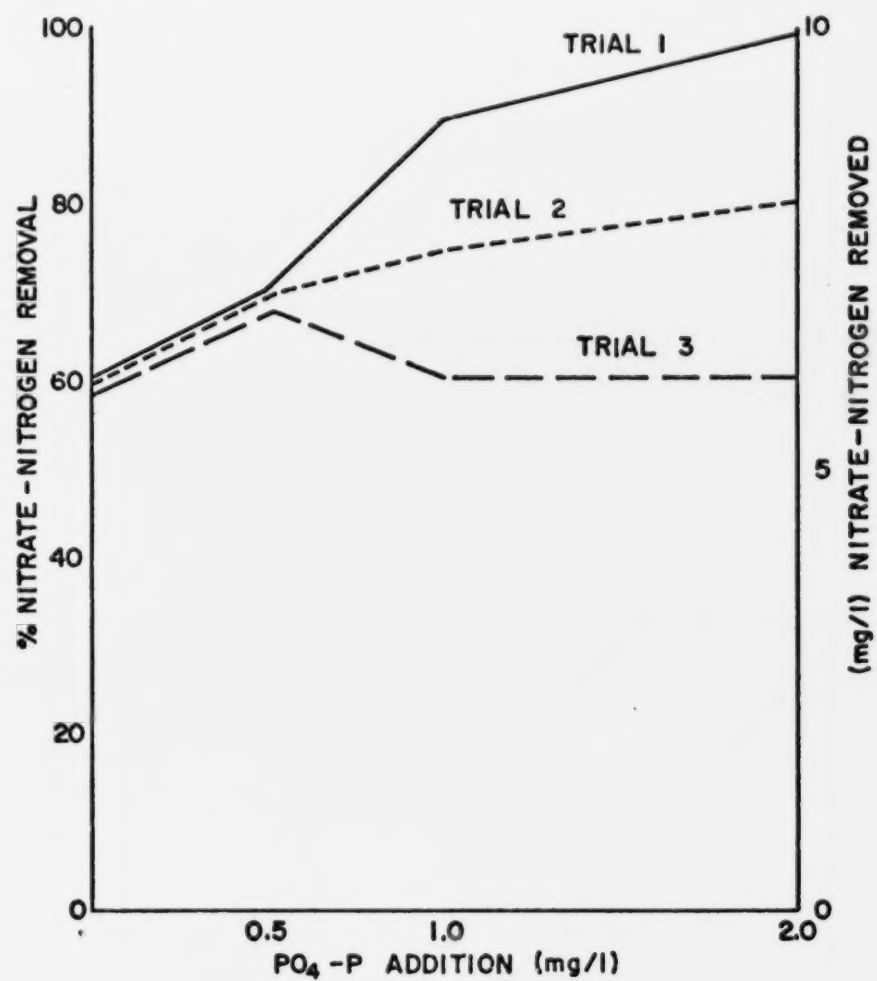


Figure 3-A. EFFECT OF FE ADDITIONS ON
ALGAL NITRATE ASSIMILATION
IN OUTDOOR GROWTH UNITS IN LATE SPRING

FIGURE 4



THE EFFECT OF PHOSPHATE ADDITION ON NITRATE REMOVAL
IN OUTDOOR GROWTH UNITS

(this is not the case with light box cultures). Figure 5 illustrates the effect of temperature on total nitrogen removal in outdoor growth units. In this particular study, a submergible heater was placed in a small growth unit for a 30-day period. Water temperatures in the unheated pond averaged 16.5°C., while the heated pond averaged 5°C. higher. Nitrogen removal rates were increased by as much as 20 percent in the heated unit over the unheated unit. The data gathered suggest cause-effect relationship between temperature and nutrient requirements, most likely due to the effects of temperature on both chemical solubility and biological activity.

Figure 6 illustrates the effect of CO₂ addition on algal nitrate assimilation in the light box. Growth rates, along with corresponding nitrogen uptake by algae, are greatly increased by the addition of 4 percent CO₂ or atmospheric air. Carbon dioxide performs two basic functions in algal systems. First, it provides the carbon necessary for cell synthesis (carbon is often a limiting nutrient in our water); and, secondly, it maintains the pH at a level at which nutrient precipitation (e.g., Fe and PO₄) is decreased.

The advisability of using CO₂ in laboratory studies of algal growth requirements is often questioned as constituting an unnatural condition. However, the function of carbon is no different from that of any other algal nutrient in that it should be in excess (unless it is specifically being tested) when the effect of any other nutrient is to be determined. Meyers (Lewin, 1967) states that the investigator faces criticism if he uses 5 percent CO₂ for aeration; yet, if he does not aerate, the CO₂ concentration may be reduced to a level below that commonly encountered in natural waters in which cell concentrations are typically low and CO₂ rarely is a limiting factor. We have found (Brown and Arthur, 1969) that in our water, when there are high algal concentrations, an external inorganic carbon source (as CO₂) acts primarily to speed up growth, rather than to change the overall effect of supplemental nutrient addition.

When extra carbon was added as 100 percent CO₂ during this past summer (1969) to several of the smaller outdoor growth units (figure 7) and the large, one-quarter acre pond for several hours each day, there was an immediate increase in nitrate, nitrite, and phosphate uptake; however, after 10 or 15 days of 100 percent nitrate removal, an algal die-off occurred in the ponds. Subsequent light box and growth unit studies have failed to reveal the cause. However, light box studies conducted immediately after the algal growth pond die-offs did indicate that neither the 100 percent CO₂ or the by-products resulting from CO₂ addition were toxic. Nor did the die-offs appear to be the result of nitrogen deficiency, as was first suspected. Furthermore, a study involving the outdoor growth units conducted in early fall (1969) showed little effect of CO₂ on nitrate

FIGURE 5

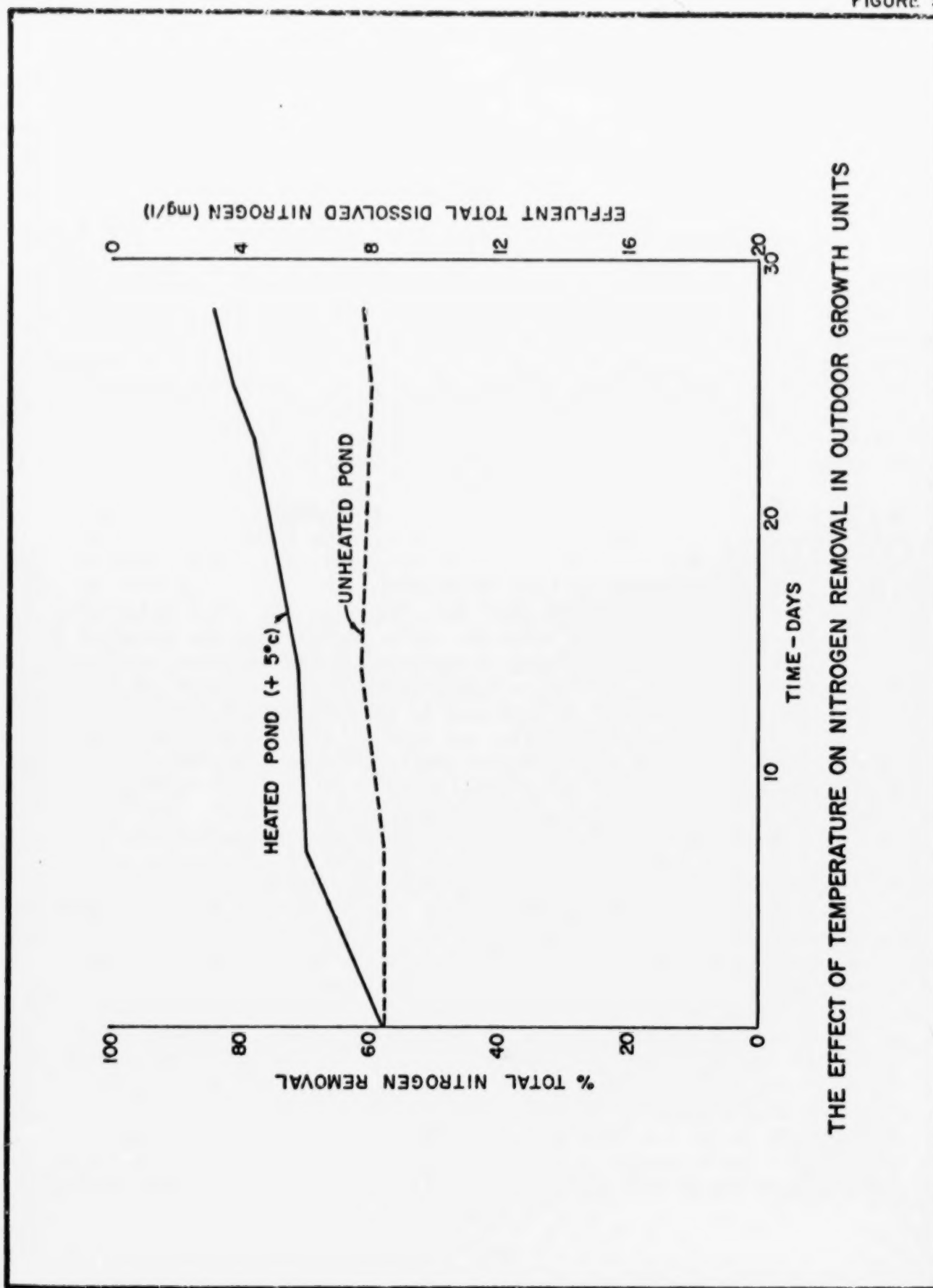
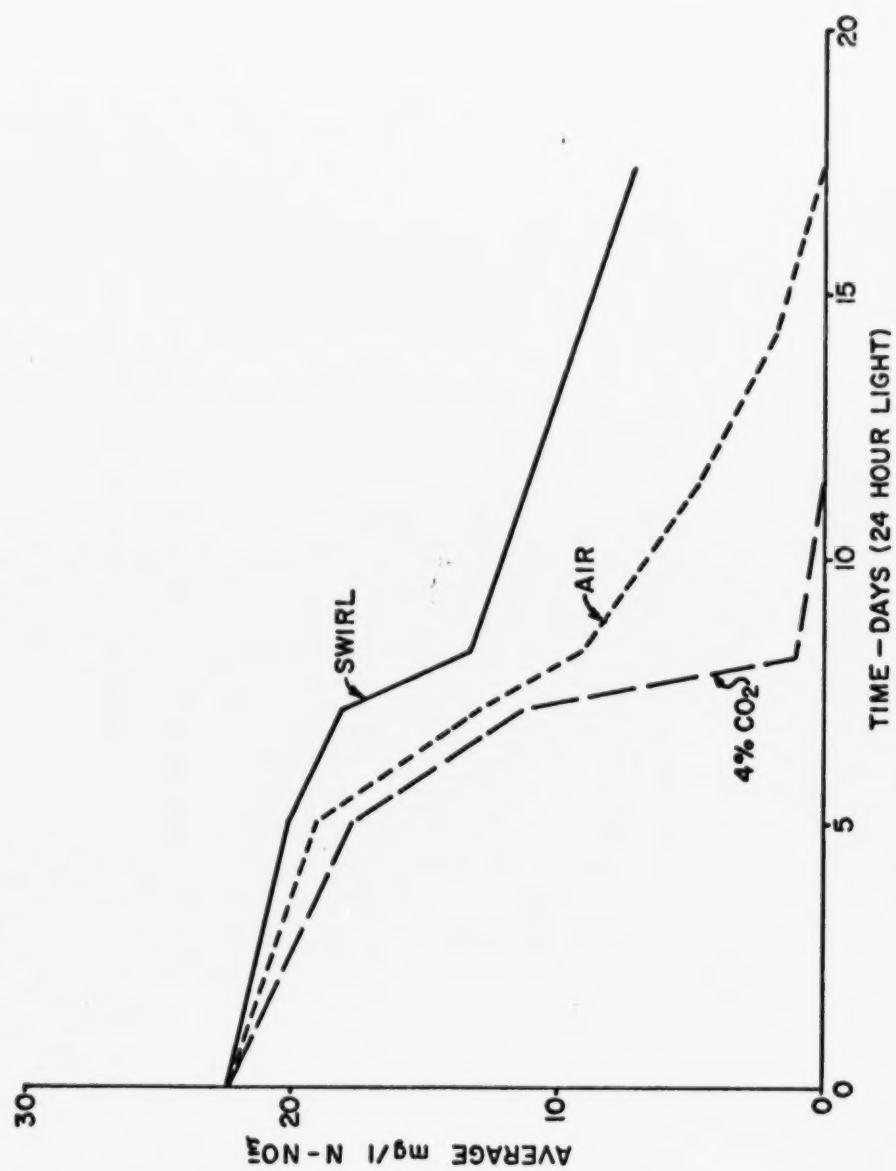
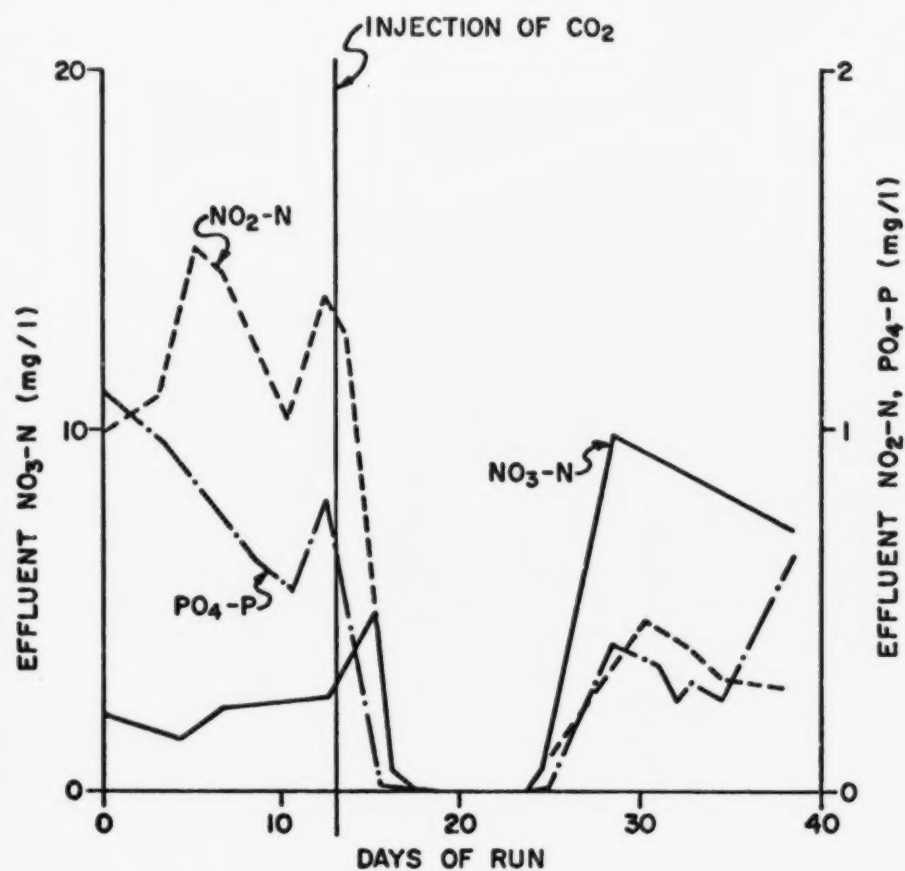


FIGURE 6



THE EFFECT OF VARIOUS LEVELS OF AERATION
ON NITRATE REMOVAL IN THE LIGHT BOX

FIGURE 7



EFFECT OF CO₂ ADDITION ON EFFLUENT NITRATE, NITRITE, AND PHOSPHATE
IN SMALL OUTDOOR GROWTH UNITS

uptake (figure 8), nor were there any subsequent algal die-offs. Indications are that the dissimilarities noted between the light box cultures and the growth units with respect to algal nutrient responses were the result of different seasonal growth rates.

Summary

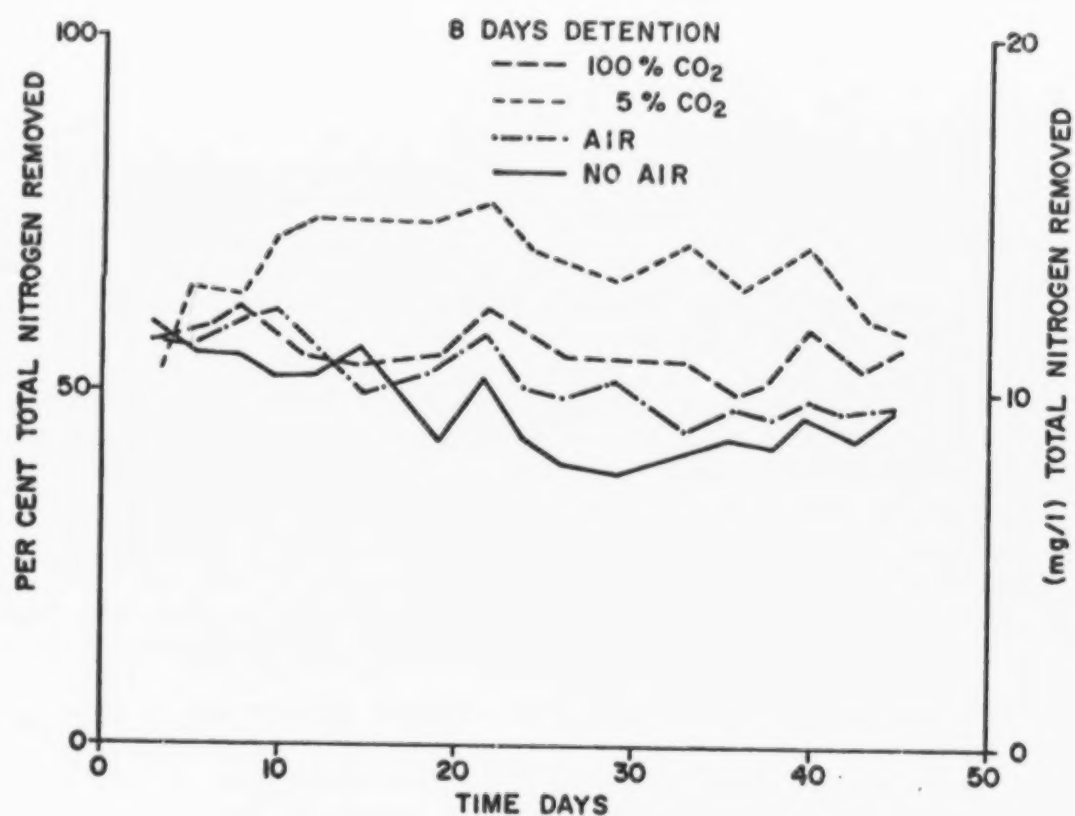
Studies presently being conducted at the IAWWTC to develop practical biological methods for removing nitrogen from the proposed San Luis Drain indicate that algal assimilation of nutrients into cellular material with subsequent removal from the growth medium is a feasible process. Furthermore, the efficiency of the proposed system is greatly enhanced if as many variables as possible are optimized, leaving only nitrogen limiting.

Earlier studies on the effect of such physical variables as detention time, mixing, and depth indicated that one or more other factors were affecting algal growth and nitrogen assimilation. Preliminary light box studies indicated that the variations which occurred in the levels of nutrients in the source water may have been responsible for differences in algal response. A review of chemical data pertaining to the source water over a 3-year period indicated that large fluctuations in major nutrients and total dissolved solids did take place.

Laboratory algal nutrient bioassays indicate that orthophosphate additions of 2.0-3.0 mg/l P are required the year round to remove 20.0 mg/l nitrate-nitrogen from the growth medium. This amount corresponds to the theoretical values predicted from analyses of the chemical constituents of typical algae. Algae usually contain 10 percent nitrogen, 1 percent phosphorus, and 50 percent carbon. Iron and carbon (as CO₂) also have been found to be limiting algal growth and nitrogen assimilation during part of the year.

Application of light box results to outdoor growth units have not always been successful. These differences are thought to be a function of growth rate. In the light box bioassays, light and temperature are optimum the year round, while in the outdoor growth units these parameters vary and as growth rates vary nutrient requirements vary. It is hoped that in the near future, it will be possible to quantify these variations and to develop relationships between them.

FIGURE 8



EFFECT OF VARIOUS LEVELS OF AERATION ON NITROGEN REMOVAL
IN SMALL OUTDOOR GROWTH UNITS

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THE EFFECTS OF NITROGEN REMOVAL ON
THE ALGAL GROWTH POTENTIAL OF
SAN JOAQUIN VALLEY AGRICULTURAL TILE DRAINAGE EFFLUENTS

By

Randall L. Brown, Richard C. Bain, Jr.,
and Milton G. Tunzi¹

Introduction

An integral part of the Firebaugh treatment studies was laboratory culture experiments to determine the effectiveness of the two biological processes under investigation, algal stripping and bacterial denitrification, for removing the algal growth potential (AGP) of the tile drainage water when added to potential receiving waters in the Sacramento-San Joaquin Delta. The AGP can be practically defined as the maximum algal growth (cell numbers, biomass, etc.) occurring in a water sample in the laboratory when available nutrients in the sample are the only limiting factors. An additional objective of these studies was to determine if nitrogen, an essential algal nutrient, was limiting in the Delta system during all seasons. Earlier work by the FWPCA (1968) had concluded that nitrogen limited algal growth only during the spring and summer.

This paper presents some results from these laboratory culture studies conducted at laboratories in Alameda (FWPCA) and Bryte (DWR), California during the period January through November 1969. General procedures for batch assays follow the Provisional Algal Assay Procedure (1969) with changes in growth being measured by either in vivo or extractable chlorophyll fluorescence (Bain, 1969). Fluorometry methods were used because of the small subsample volumes required for chlorophyll measurement and because of their simplicity, rapidity, and sensitivity.

Methods and Materials

Water. Samples of Delta water were collected near Antioch the day before an experiment and stored overnight in the dark in plastic bottles. Treated and untreated tile drainage was also obtained from the Firebaugh site the same day. Algae were removed from growth

¹ Biologist, California Department of Water Resources, Fresno, California, and Sanitary Engineer and Aquatic Biologist, Federal Water Pollution Control Administration, Alameda, California, respectively.

pond effluent using a flocculent, usually alum or lime. This separation process simulated conditions of an operating algae harvesting plant. All samples from the Firebaugh site were filtered through Whatman GFA glass filters to remove residual fluorescence. The Delta samples were unfiltered and thus contained native phytoplankton which was tested for growth response in the assay. Unfiltered Delta water, usually containing 1,000-2,000 algal cells per milliliter (predominantly diatoms), was mixed with various proportions of treated and untreated agricultural drainage water. Algal counts of representative flasks were obtained at the termination of an experiment.

Environmental Conditions. Although both laboratories generally followed culture procedures outlined in the Provisional Algal Assay Procedure (1969), there were deviations because of preexisting facilities and equipment. In each laboratory, growth chambers were constructed in converted cold storage boxes with temperatures controlled to $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Lighting was provided by cool-white fluorescent bulbs of 350-450 ft-c illumination. At Alameda, light was directed from beneath the flasks; whereas, at Bryte the bulbs were above the cultures. Lighting was continuous at both laboratories. Bryte had reciprocating shakers and both laboratories had the facilities for air mixing; however, only daily swirling was used in these regrowth studies. Preliminary culture work indicated that swirling was as effective as either shaking or air mixing. The cultures were incubated in 500 ml Erlenmeyer flasks filled with 250-300 mls. of sample. All cultures were grown in triplicate.

Measurement of Response. Both laboratories utilized Turner Model III fluorometers to measure the in vivo changes in chlorophyll fluorescence. Modifications to the fluorometers included a red sensitive photomultiplier and high sensitivity door (which passes light through the sample more than once) at Bryte and blue light sources at both laboratories. A blue primary filter (Corning CS 5-60 with maximum transmission at 450 mμ) and a red secondary filter (Corning CS 2-64, maximum transmission at 650 mμ) were used in the machines. Instruments were nulled against distilled water blanks and subsamples read using 12x75 mm cuvetts. Because of the greater sensitivity of the instrument at Bryte, samples with off-scale readings were diluted with distilled water to bring them back to a readable range. As much as possible all samples were read on the same sensitivity scale.

In vivo fluorometry was used after June 30, 1969. Before this time, growth was measured by the fluorescence of acetone extracts. In this method the water sample was filtered through a Whatman GF/C glass filter, preserved with magnesium carbonate, frozen, and stored in darkness. The entire filter (with algae) was then ground in a tissue grinder with 90 percent acetone. The chlorophyll dissolved in the

90 percent acetone was measured by fluorometry. Chlorophyll "a" was distinguished from phaeophytin by a second reading after the addition of HCL.

Although fluorescence was the principal parameter recorded, on occasion other data were obtained. Nitrate, pH, absorbency at 410 mu, and volatile solids information was obtained during some runs.

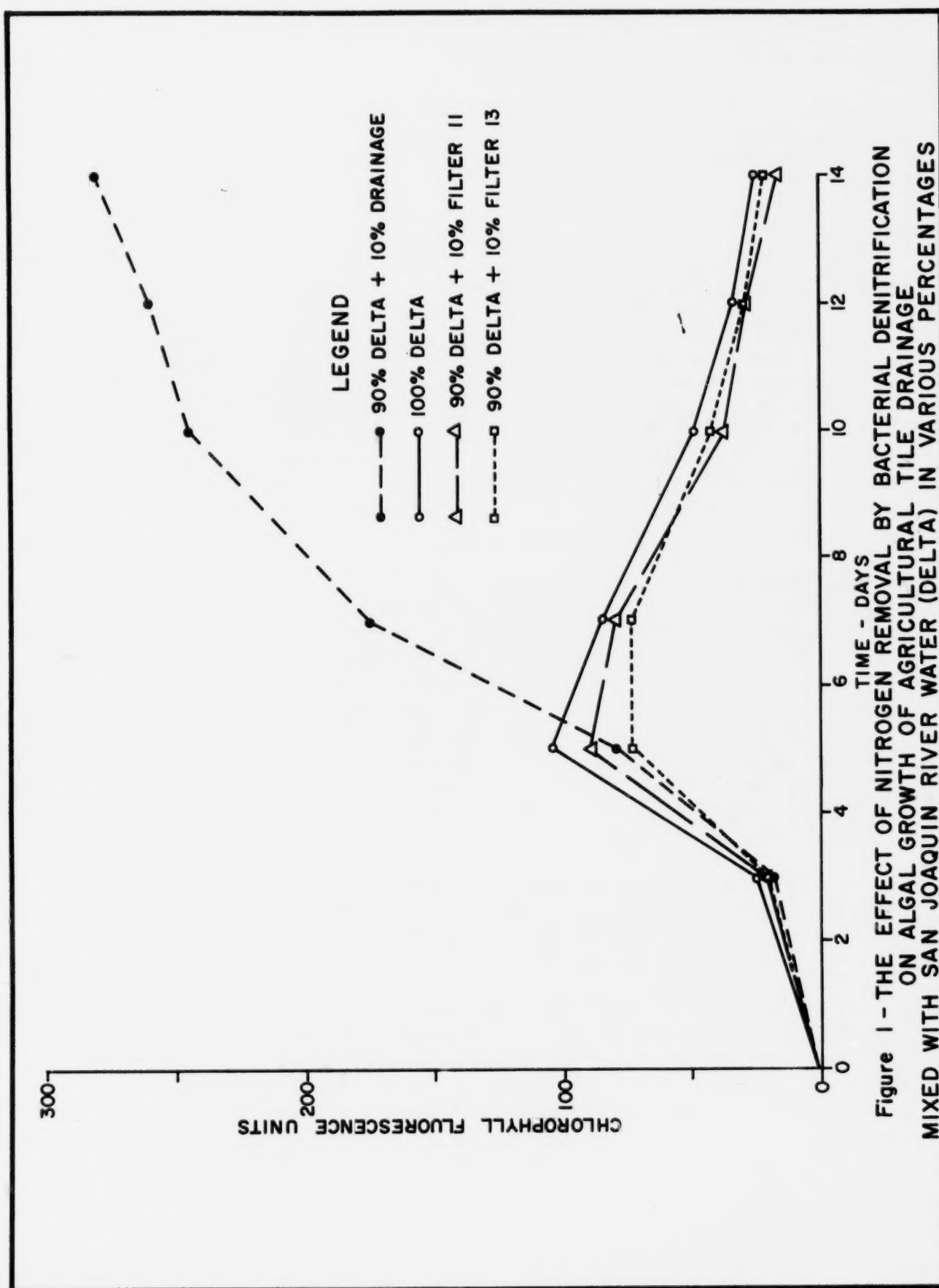
Results

Growth Limiting Nutrient. The primary objective of one series of experiments was to demonstrate that removal of nitrate from agricultural waste water would reduce its algal growth potential. Figure 1 shows the results of 10 percent additions of agricultural drainage water before and after bacterial denitrification processes. Algal growth in those cultures containing processed water was almost identical to Delta water controls. In contrast, the addition of untreated drainage promoted continuous growth much beyond that of the other samples. Concentrations of $\text{NO}_3\text{-N}$ in these samples was 17.9, 0.2, and 0.6 mg/l for the untreated water and for the two tested bacterial filters, respectively.

Adding nitrogen back to the water from which it has been removed will result in a medium with an algal growth potential similar to the original agricultural waste water. Figure 2 illustrates typical results of nitrogen re-addition to treated waste water. The addition of 5 percent bacterial filter water had a slight stimulatory effect on the algal growth potential of the Delta water. A 5 percent addition of untreated drainage water resulted in a peak fluorescence value of approximately 200. Additions of 3 or 6 mg/l nitrogen (NaNO_3) to the treated water caused the AGP of these samples to reach peak values similar to that of the untreated water. Untreated drainage water had a nitrate concentration of approximately 14 mg/l.

Waters with the chemical composition shown in table 1 gave the algal bioassay results in figures 3 and 4. The treated and untreated agricultural waste water was added to San Joaquin River (Delta) water at concentrations of 2, 5, and 10 percent by volume.

In figure 3 the AGP's for effluent from the bacterial filter and the untreated agricultural drain are compared. The AGP's for the combinations of untreated drain water are all significantly higher than those with effluent from the filter. Using the data from table 1, the actual increases of inorganic nitrogen (nitrate, nitrite, and ammonia) range from 0.3 to 1.6 mg/l with untreated agricultural tile drainage water addition and from 0.012 to 0.06 mg/l increase with bacterial filter effluent. Apparently the addition of more



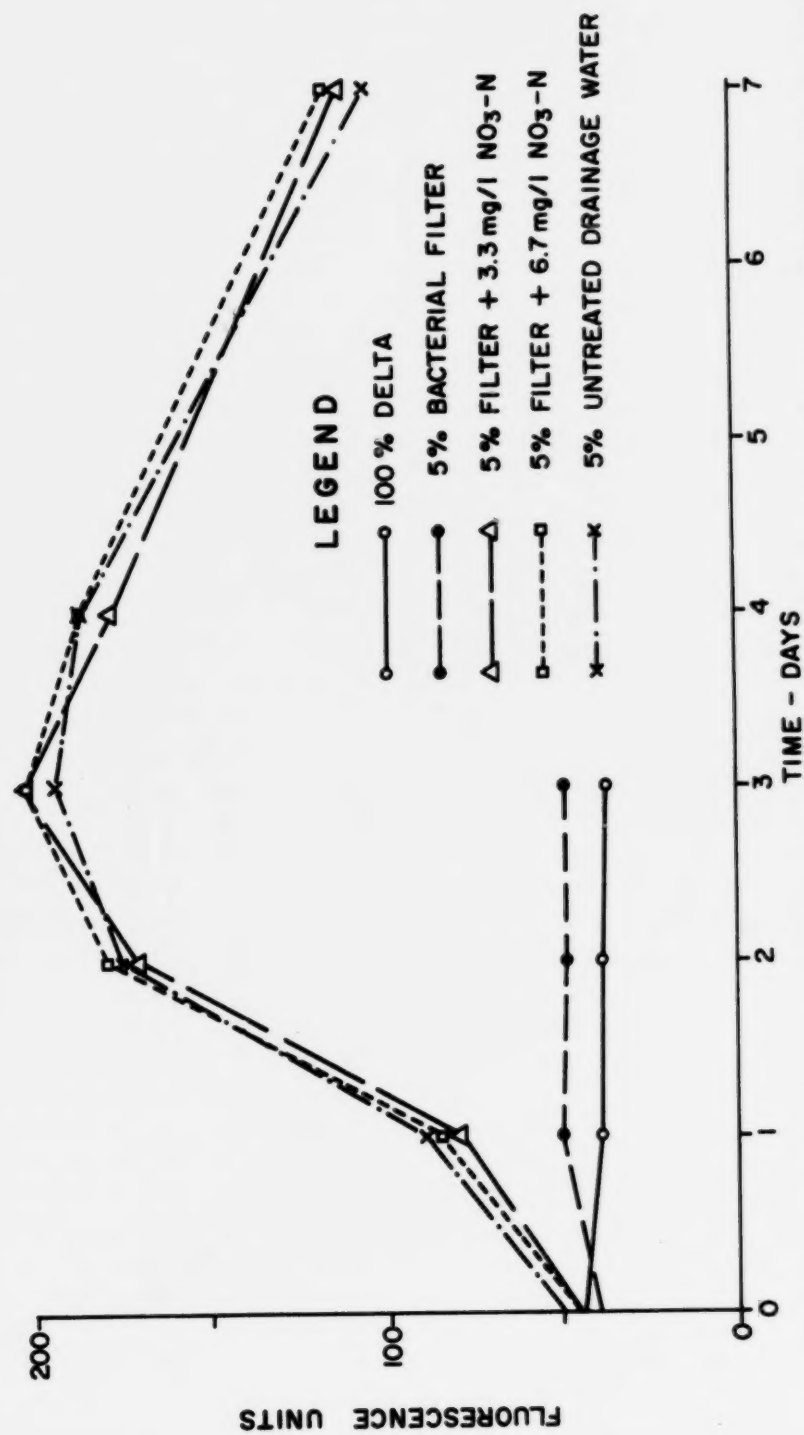


Figure 2 - THE EFFECT OF NITRATE-NITROGEN ADDITIONS ON ALGAL GROWTH RESPONSES IN CULTURES OF TREATED AGRICULTURAL DRAINAGE WATER MIXED WITH SAN JOAQUIN RIVER WATER (DELTA).

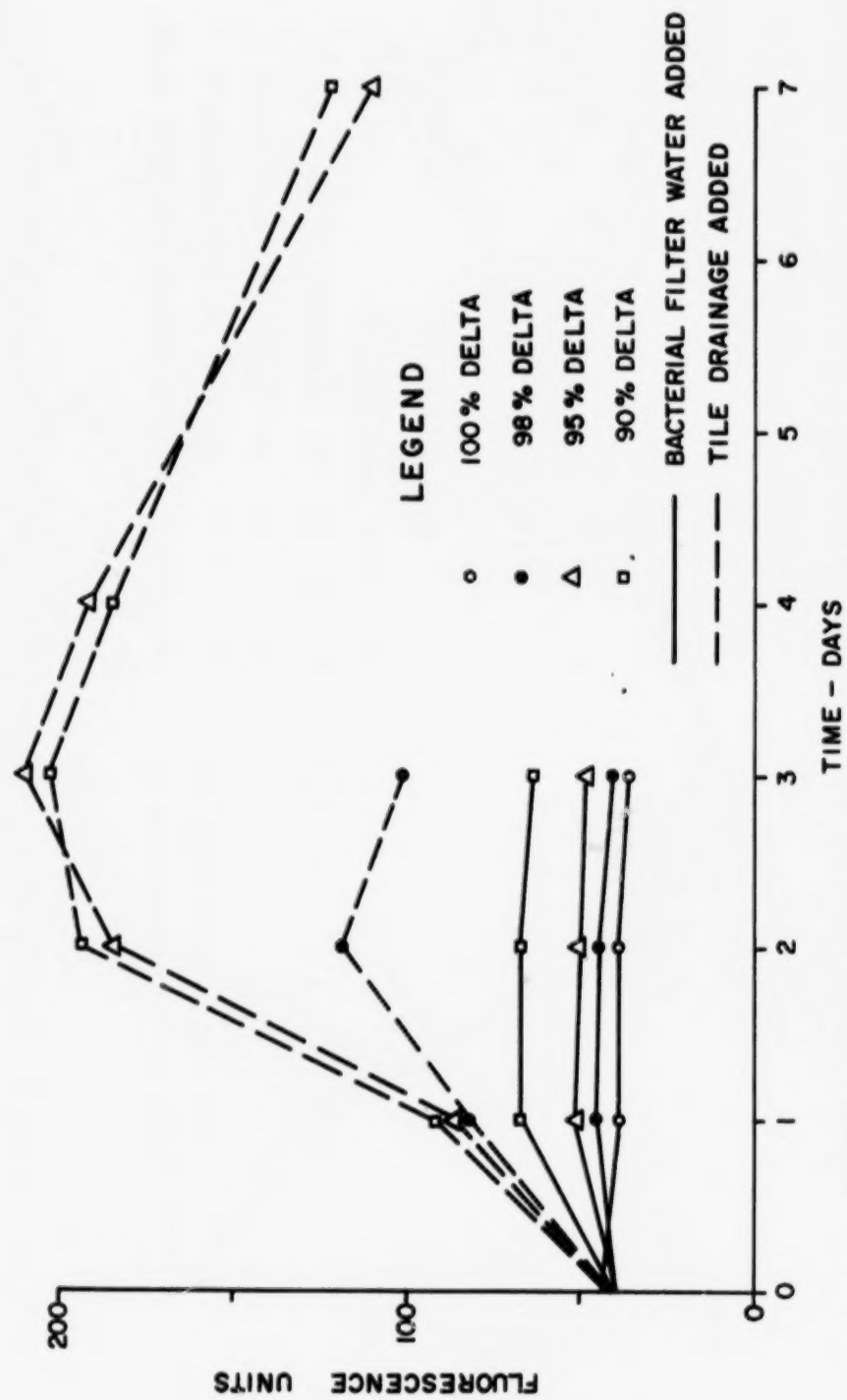


Figure 3 - ALGAL GROWTH RESPONSES OF VARIOUS COMBINATIONS OF UNTREATED AGRICULTURAL TILE DRAINAGE AND BACTERIALLY DENITRIFIED WATER MIXED WITH SAN JOAQUIN RIVER WATER (DELTA)

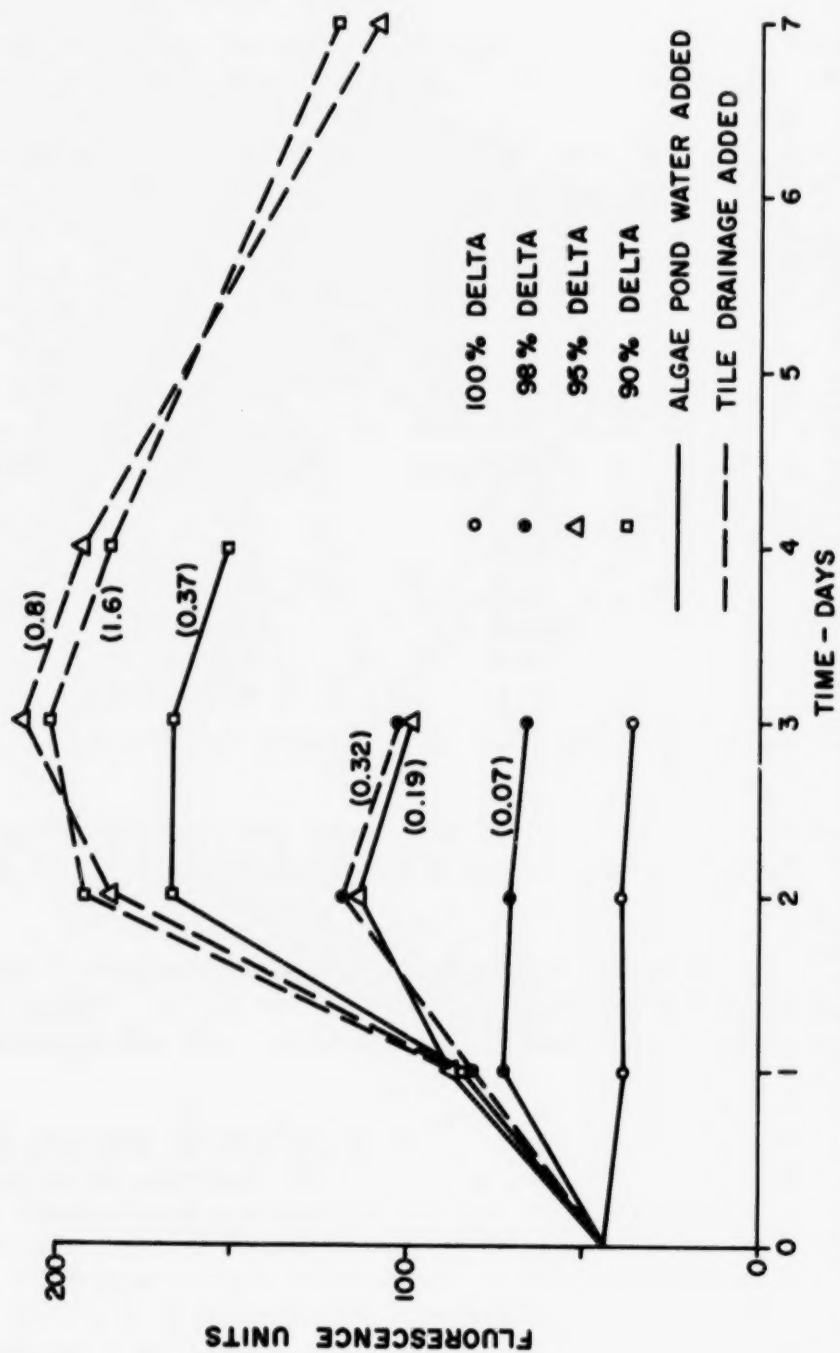


Figure 4 - ALGAL GROWTH RESPONSES OF VARIOUS COMBINATIONS OF UNTREATED AGRICULTURAL TILE DRAINAGE AND "ALGAL STRIPPED" WATER MIXED WITH SAN JOAQUIN RIVER WATER (DELTA). TOTAL INORGANIC NITROGEN (mg/l) IN THE SAMPLES ARE IN PARENTHESES ADJOINING THE APPROPRIATE

than 0.8 mg/l $\text{NO}_3\text{-N}$ (5 percent agricultural drainage water) was enough to cause the maximum increase in growth because the curves for 5 and 10 percent drain tile water additions are essentially the same. The stimulation effect produced by the filter effluent would probably not normally be noted in the Delta water but in this case the original Delta water nitrogen levels were so low that addition caused stimulation of growth.

Figure 4 shows a comparison of the bioassays of effluents from the untreated drainage and from the algal stripping system. The total inorganic nitrogen concentration in the algal effluent was higher than in the bacterial filter effluent, 3.73 mgN/l compared to 0.62 mgN/l (table 1).

Table 1 - Chemical Data for Firebaugh Samples
September 29, 1969

Chemical	Untreated Agricultural Tile Drainage Water (mg/l)	Treated Agricultural Tile Drainage Water	
		Algal Pond (mg/l)	Bacterial Filter (mg/l)
$\text{NO}_3\text{-N}$	16.3	3.4	0.3
$\text{NO}_2\text{-N}$	0.0	0.2	0.2
NH-N	0.0	0.13	0.12
Total Inorganic N	16.3	3.73	0.62
Organic N	0.4	1.19	0.48
$\text{PO}_4\text{-P}$	0.1	0.1	0.1

The concentration of nitrogen in the algal pond effluent was about 2-3 times as high as would normally be discharged from the treatment facilities.

In figure 4, each bioassay curve has the total inorganic nitrogen concentration present in the sample yielding the curve. Note the direct functional relationship between fluorescence peak and nitrogen concentration.

Comparison of Treatment Methods. The organisms in the two treatment methods use entirely different pathways for removing nitrogen. Therefore, there was a possibility that the product waters might have differing effects on AGP even when their nitrogen contents were similar in concentration. This possibility was enhanced by the algal separation process which might remove trace metals or other growth requirements from solution. Although many assays were conducted, it was often impossible to obtain process effluents with similar nitroge

concentrations. Thus it was difficult to show if either system was more effective in lowering the algal growth potential of the agricultural waste water based on their nitrogen content alone. Generally, it can be stated that nitrogen removal lowered the AGP, regardless of what treatment method was used. Two experiments in which the effluent nitrogen levels were comparable also indicate that the two systems were similar in their effect on AGP.

The first experiment was conducted on July 25, 1969, using effluent from an algal pond and a bacterial filter having total nitrogen concentrations of about 1.5 mg/l, but with less than 0.5 mg/l inorganic nitrogen. Analysis of variance calculations was performed on differences between initial and maximum fluorescence readings. Table 2 shows the 95 percent confidence levels obtained by a multiple range test. The samples connected by underlines are not different at the 95 percent confidence level. In all instances both pond and filter effluents showed significantly lower effect than sump water addition. The pond and filter effluents were the same at 1 and 10 percent additions, but the algae had a greater nutrient removal effect at 20 percent addition. Based on nitrogen data both effluents should have had the same effect at all dilutions.

Table 2 - Comparison of Growth Response in San Joaquin River Water With Percentage Additions Of Algal Pond, Bacterial Filter, and Untreated Tile Drain Water

Percent Addition	Untreated Agricultural Tile Drain Water	Treated Agricultural Tile Drain Water	
		Algal Pond	Bacterial Filter
		(Fluorescence units)	
1%	10.8	1.2	1.2
10%	37.3	1.2	2.4
20%	34.9	0.0	14.4

Another experiment conducted on September 25, 1969, again using water from the algal and bacterial filter systems with less than 0.5 mg/l inorganic tended to confirm the hypothesis that both methods of treatment affected AGP in a similar manner (table 3). Again the difference between peak and initial fluorescence of the various percentages of treated water were lower than noted in comparable percentages of untreated water. In this study algal and bacterial effluents were no different in their effect on algal growth at any dilution at the 95 percent confidence level.

Table 3 - Comparisons of Growth Response In
San Joaquin River Water With Percentage
Additions of Algal, Bacterial, and Untreated
Tile Drain Water
September 25, 1969

Percent Addition	Untreated Agricultural Tile Drain Water	Treated Agricultural Tile Drain Water	
		Algal Pond	Bacterial System
		(Fluorescence units)	
1%	4.2	1.3	3.0
10%	36.2	3.0	1.9
20%	39.8	1.1	1.9

Seasonal Variations in San Joaquin River Water at Antioch. The chlorophyll fluorescence of Antioch water increased from 22.5 fluorescence units in mid-June to a peak of 32.5 in late July and gradually declined to a value of 16.4 by mid-November. Nitrate nitrogen tends to be lowest in summer and increase in the fall reflecting the seasonal reductions in algal crop (see table 4).

When Antioch samples are incubated in the laboratory, the chlorophyll values achieved are similar for all the months tested; see table 4. Spring and fall samples exhibit growth indicating presence of inorganic nutrients in the Antioch water; summer samples exhibited little or no growth between initial (field) values and laboratory incubated values made over a period of 1 week or more. This lack of additional yield during summer suggests nutrients were essentially exhausted in the Delta waters sampled during summer. This finding agrees with past findings by FWPCA in connection with San Joaquin Master Drain studies, (Bain, et al., 1968).

Table 4 - Seasonal Chlorophyll and Nitrate Variations
in the San Joaquin River at Antioch Bridge

Date Sampled	Chlorophyll Fluorescence ^a		NO ₃ -N (mg/l) (initial)
	Initial (field)	Peak (AGP)	
Nov. 14, 1968	0.3	27.7	--
Dec. 13, 1968	1.6	34.5	.43
Jan. 4, 1969	1.0	30.8	.61
Jan. 28, 1969	1.2	82.6	.74
Feb. 14, 1969	0.9	54.9	.95
Mar. 10, 1969	1.4	36.2	.53
Apr. 4, 1969	3.3	12.1	.22
June 18, 1969	22.5	30.9	.18
July 25, 1969	32.5	32.5	.04
Aug. 18, 1969	27.6	28.0	.05
Sept. 9, 1969	24.6	26.5	.08
Sept. 29, 1969	25.4	28.3	--
Oct. 20, 1969	21.6	28.2	.00
Nov. 17, 1969	16.4	25.5	.22

^a Direct readings at 30X scale. Values before June 1969 were corrected from extracted samples based on sample splits to determine conversion factor.

Discussion

Algal growth potential tests in two different laboratories indicate that nitrate-rich agricultural drainage, when mixed with San Joaquin River Delta water, stimulates algal growth. Seasonal factors do not alter this finding although *in situ* algal crop levels vary seasonally in the Delta. Control samples from the Delta near Antioch yielded approximately equal chlorophyll peaks in 14 separate AGP experiments during a 1-year period.

The waters of the Delta near Antioch vary seasonally in nitrate-nitrogen concentration. Summer nitrate concentrations of 0.05 mg/l or less, as nitrogen, produced no significant chlorophyll increases in AGP tests, suggesting nutrient limitations in these waters. Additions of nitrate-rich tile drainage increased chlorophyll in all experiments. Additions of nutrient stripped effluents from different pilot scale treatment facilities at Firebaugh, California, produced no additional growth except in cases where nutrient removal efficiencies were known to be low. Selective removal of nitrate-nitrogen by anaerobic denitrification or removal of nutrients by algal cells grown in shallow ponds yielded comparable bioassay results.

The Firebaugh experience suggests that eutrophication due to agricultural waste waters can be controlled by treatment. The experiments do not pretend to forecast receiving water response, but to promote further evidence concerning the importance of nitrogen nutrition in controlling western Delta algal populations. The AGP tests are useful ways to demonstrate tertiary treatment efficiency, particularly since they measure the effect of treatment on eutrophication symptoms.

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HARVESTING OF ALGAE GROWN IN AGRICULTURAL WASTE WATERS

By

Bruce A. Butterfield and James R. Jones¹

Introduction

The U.S. Bureau of Reclamation, the Federal Water Pollution Control Administration, and the California Department of Water Resources are currently engaged in a joint study near Firebaugh, California, to determine the feasibility of removing nutrients from subsurface agricultural waste water in the San Joaquin Valley. Algae harvesting is being studied for three reasons. One of the processes being studied is to grow algae, under controlled conditions, which assimilates the unwanted nutrients into cellular material, and then to harvest the algae from the suspension. Secondly, removal of naturally occurring algae will be necessary because disposal into the San Joaquin Delta-San Francisco Bay System is not desired. And finally, if anaerobic denitrification columns are used to remove nitrogen, it will be essential to remove algae before the drain water enters the unit.

This paper is concerned with the algal removal or separation studies carried on at the Interagency Agricultural Waste Water Treatment Center (AWWTC). The studies were divided into two phases. One phase was concerned with the laboratory evaluation of commercially available flocculating aids. The other phase, with evaluation of some commercially available separation devices.

Flocculation-Sedimentation Study

Methods and Materials. In the laboratory evaluation of commercially available flocculating aids, the source of algae-laden water was the outside growth units of the AWWTC. The algae were grown in saline water (total dissolved solids has a yearly range from about 2,000 to over 8,000 mg/l) with some nutrients added to encourage algal growth. The predominate algae grown were Scenedesmus quadricauda. Concentrations ranged from approximately 150 to 400 mg/l as volatile solids. A day's sample was collected in a large container and stored in a dark, cool place. Subsamples were extracted from it throughout the day. This was done to eliminate daily variations and to allow comparison between different flocculants.

¹ Assistant Civil Engineer, California Department of Water Resources; Civil Engineer, U.S. Bureau of Reclamation, Department of the Interior, respectively; Fresno, California.

In jar tests described below, a total of 56 flocculation aids were tested alone and in conjunction with these flocculants; aluminum sulfate, calcium hydroxide and ferric sulfate. The subsamples with varying flocculation aid concentrations were prepared simultaneously and then allowed to settle for 1 hour in a cool, dark cabinet. The next step was to decant and measure percent light transmittance of the supernatant. Percent transmittance was scaled from zero percent (total darkness) to 100 percent (distilled water) using a spectrometer at 410 mu. The percent transmittance and total volatile solids of the uncoagulated sample were also measured. With these two values, a ratio was developed indicating the amount of algae removed per sample. The testing of the flocculation aids was accomplished by optimizing mixing time and rate of mix for the main flocculants. The criteria were 70 r.p.m. and 3 minutes for aluminum sulfate and 40 r.p.m. and 8 minutes for calcium hydroxide. If used alone, they were mixed the same as aluminum sulfate. These values were obtained using an 800 milliliter sample in a one-liter beaker mixed by a multimixer with 3-inch by 7/8-inch rectangular paddles.

Discussion

Of the 168 combinations tested, 60 did show some benefit in the separation process; however, economic evaluation (cost of flocculation aid required) indicated that only the following 24 combinations warrant further investigation:

<u>Flocculation Aid</u>	<u>Main Flocculant</u>
1. Dow Chemical Co. PEI 600	aluminum sulfate
2. Dow C-31	none
3. Dow C-31	aluminum sulfate
4. Dow C-32	none
5. Dow C-32	aluminum sulfate
6. Narvan Mines Zeta Flocc "O"	calcium hydroxide
7. Nalco Nalcolyte 603	aluminum sulfate
8. Nalco Nalcolyte 610	calcium hydroxide
9. Rohm and Haas Primafloc C-3	aluminum sulfate
10. Rohm and Haas Primafloc C-5	none
11. Rohm and Haas Primafloc C-5	aluminum sulfate
12. Rohm and Haas Primafloc C-7	none
13. Hercules, Inc. Hercofloc 814	aluminum sulfate
14. General Mills, Inc. Genfloc 155	none
15. General Mills, Inc. Genfloc 155	calcium hydroxide
16. General Mills, Inc. Genfloc 156	none
17. General Mills, Inc. Genfloc 156	calcium hydroxide
18. General Mills, Inc. Genfloc 162	none
19. General Mills, Inc. Genfloc 162	calcium hydroxide

Flocculation AidMain Flocculant

20. American Cyanamid Co. Magnifloc 521-C	none
21. American Cyanamid Co. Magnifloc 521-C	aluminum sulfate
22. American Cyanamid Co. Magnifloc 820-A	calcium hydroxide
23. American Cyanamid Co. Magnifloc 836-A	calcium hydroxide
24. American Cyanamid Co. Magnifloc 835-A	calcium hydroxide

The performance of the three main flocculants varies throughout the year. At certain times, ferric sulfate was tested and found to be cheaper and perform better than either aluminum sulfate or calcium hydroxide. At present, they are being monitored on a weekly basis in order to determine which would be the most economical. Since iron in the form of ferric chloride (also a flocculant aid) has been added to the algae growth units as a nutrient, aluminum sulfate and ferric sulfate have become more effective and calcium hydroxide less effective.

Carbon has been added to the growth units in the form of carbon dioxide and has also affected the efficiency of these three flocculants. Carbon dioxide addition lowers pH, causing ferric and aluminum compounds to become more effective and calcium hydroxide less effective. At the AWWTC, a 5.6 pH was found to be optimum, when ferric and aluminum compounds are used; but this is uneconomical due to the cost of acid.

Seasonal variations of water quality, temperature, light, etc., appear to be influencing factors and must be monitored. A typical effective series of tests performed in the spring, of aluminum sulfate, ferric sulfate, and calcium hydroxide is shown on table 1.

Table 1 - Flocculant Effectiveness
(in percent transmittance)

Flocculant	Flocculant Concentration, mg/l						
	0	3	5	10	20	40	80
Ferric Sulfate	63	88	94	94	95		
Aluminum Sulfate	63	64	65	66	74	94	
Calcium Hydroxide	67	66	66	67	70	93	95

The percent transmittance of the original sample was 6 percent and the volatile solids were about 500 mg/l. The zero concentration shows the effect of ferric chloride addition to the growth pond; however, no carbon dioxide was being added then.

Pilot Harvesting Studies

The second phase of separation studies involved the evaluation of pilot-scale separation devices. The units included flocculation and settling units, centrifuges, a microscreen, a vacuum filter, a rapid sand filter, and sand drying beds. It was planned that these units would give an indication as to how traditional separation equipment would work on algae-laden water at the AWWTC.

The algal concentration of growth pond effluent varies from 150 mg/l to 400 mg/l (0.015 to 0.04 percent by weight). Algae separation is divided into three stages: concentrating, dewatering and drying. Concentrating increases the algae solids to 1-to-4 percent. Dewatering increases the solids to 8-to-16 percent. Drying processes bring the solids to 85-to-92 percent. Destruction of the algae cell and denaturing of the protein occurs when drying exceeds approximately 92 percent.

Flocculation and Sedimentation. Algae at Firebaugh can be concentrated to about 1 or 2 percent by weight through flocculation and sedimentation. Settling as a procedure for harvesting of algae is hindered by the small size of Scenedesmus quadricauda (10-40 micron) and its specific gravity (approximately 1.006). Auto-flocculation, the tendency for algae to clump together and settle, occurred naturally under certain conditions in the rapid growth pond.

A complete self-contained water treatment plant was used for concentration studies. Installed in the settling chamber was a modular unit of 1-1/2-inch-diameter settling tubes at a five degree inclination to the horizontal. The tubes were installed to reduce the settling distance of the algae. When the tubes were drained or backwashed, the algae sludge flowed down and out of the inclined tubes.

In general, when transmittance of the settling tank effluent fell below 90 percent transmittance the unit was backwashed. The amount of water needed to backwash the tubes was 5-10 percent of the product water and contained less than 1 percent algae by weight. Aluminum sulfate was used as a flocculation aid in the unit. With an influent pH above 9.0 and detention time of 2 hours, 300 to 400 p.p.m. of aluminum sulfate were needed to remove the suspended algae during the fall.

Upflow Clarification. One of the concentration devices tested at the AWWTC was an upflow clarifier. As algae-laden water flows upward, the cross-sectional area increases and the velocity decreases causing a settling to take place. At this point, a blanket of floc developed causing a filtering effect. The sludge or concentrate was drawn off at this point and clarified liquid was passed off at an upper level.

The operation involved pH adjustment (to approximately 10.8) of the influent with sodium hydroxide to flocculate the suspended solids. At times the blanket appeared to plug the unit and stop all flow. This was followed by a breakup of the blanket and short-circuiting. The operation removed 90 to 95 percent of the suspended solids in the 2 to 4 percent solids concentration range.

Centrifugation. Investigations were made into the application of a solid bowl continuous horizontal centrifuge and a yeast-type nozzle centrifuge. A self-cleaning centrifuge, similar to the yeast separator but with added features, will be tested.

The centrifuges were tested both as algae concentrators and dewaterers. The dewatering study used algae water concentrated in a sedimentation unit using aluminum sulfate. A progressing cavity pump or a gravity feed system was used in all cases to provide a steady, nonpulsing flow.

The solid bowl centrifuge tested was a 6-inch pilot unit. Variables included flow rate centrifugal force, and depth of liquid in the bowl. The bowl depth controlled the sludge consistency from high flow and wet cake (higher efficiency of algae removal) to low flow and dryer cake (lower efficiency). In general, algae concentrations of 3 to 22 percent by weight were achieved, but the efficiency was usually less than 10 percent. An efficiency of 28 percent was achieved, but with high flow and wet cake. Whether used for concentrating or dewatering, the efficiencies were comparable, but due to the large volume that will need concentrating, it would not be economical to use a solid bowl centrifuge except for dewatering. The solid bowl centrifuge was found to be relatively maintenance-free.

The yeast-type nozzle centrifuge is designed for solid/liquid and solid/liquid/liquid separation with continuous feed and removal. Centrifugal force is constant and the solids discharge is controlled by varying the number and size of nozzles. Maximum flow rate was 1-1/2 g.p.m. With flow rate below 1/2-gallon per minute, no removal was achieved due to lack of cake buildup in the bowl. As a primary concentrator this unit obtained removals greater than 80 percent, but would soon plug with algae and suspended clay material. As a dewaterer, it would plug sooner with the heavier algal loading.

Screening. A vacuum filter and microscreen are being evaluated. The vacuum filter has not been tested sufficiently to make any conclusions. In conjunction with this unit, a leaf kit filter was supplied to help in evaluating the effectiveness of different filter material. A close-weave monofilament nylon material (120 by 240 threads to the inch) showed promise in separation and was relatively easy to clean which is an important factor in economics. Several synthetic felts gave acceptable results.

An automatic, rotating, drum-type, straining system was tested for separation of algae. The unit consisted of a self-contained 4-foot-diameter by 1-foot-wide rotating drum. Screens of 25 micron and 35 micron were supplied with the unit. Algal-laden water entered the interior of the partially submerged drum and was strained as the water flowed outward through the revolving screen. The algae was caught on the screen and washed off by a row of water jets located above and outside the drum. It became apparent that the 25 micron screen allowed the smaller algal cells to pass. With the 25 micron screens, the unit removed up to 8 percent of the algae in a slurry flow of approximately 1 percent of the total influent.

Rapid Sand Filtration. A cross-flow sand filter was evaluated as a primary algal concentrator. This filter consisted of two sand beds $\frac{3}{8}$ inch thick, 5 inches wide, and 5 feet high. The sand was contained between two pieces of fine-weave nylon monofilament cloth, which was supported by $\frac{3}{8}$ inch wide plastic spacer strips. The raw water was pumped up between front and back plastic covers in the space formed by the plastic spacer strips. It then passed through the sand bed from both sides toward the center open space provided by more $\frac{3}{8}$ -inch spacer strips. The product filled a column above the filter and overflowed at the top. The water in the column was used to backflush the filter when the pressure difference through the sand bed reached a predetermined level. It became apparent that the sand bed was becoming plugged with algae as the time between backwashes became shorter. The algae removal was over 90 percent (without chemical addition) and the solids content of the sludge, or backwash, was as high as 10 percent.

Future Work

The objective during the next year will be to monitor seasonal variations that affect the harvesting of algae and to refine operational procedures. Seasonal monitoring for chemical requirements will be maintained. Additional seasonal monitoring of the physical characteristics of algae will be maintained to extend the evaluation of hardware in the dewatering and drying processes. The evaluation of the microscreen and vacuum filter will be continued to test various filter materials. A self-cleaning basket centrifuge will also be evaluated. Future separation work will include flotation studies.

Conclusions

Through laboratory and field testing, it is obvious that effective concentration can be accomplished using the flocculation-sedimentation process to remove 90-95 percent of the suspended solids from algae-laden agricultural waste water. It appears that dewatering and

drying can be accomplished but the efficiencies of the units tested at AWWTC were low. The need to recirculate the water would increase the overall cost; however, it is believed better results will be achieved in larger capacity units.

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COMBINED NUTRIENT REMOVAL AND
TRANSPORT SYSTEM FOR TILE DRAINAGE
FROM THE SAN JOAQUIN VALLEY

By

Joel C. Goldman, James F. Arthur,
William J. Oswald, and Louis A. Beck¹

Introduction

Current plans call for treatment of agricultural waste water for nutrient (nitrogen) removal from the proposed San Luis and Master Drains prior to discharge into the Bay-Delta Area. Of the several treatment processes currently being investigated, the algae stripping process was estimated to have required between 6,000 and 12,000 acres of land to accomplish this task. The original proposal for utilizing the algae process considered only the use of a separate treatment facility to be located adjacent to the Drain somewhere along its length. Because every body of water is a potential algal growth system, this proposal will demonstrate that there are several alternatives to the original plan, which will greatly reduce the total cost of treatment and perhaps improve the overall efficiency of nutrient removal.

General Aspects of Proposal

Objective. It is the objective of this report to present alternate solutions for the treatment of drainage water through the use of In-Line Treatment. This treatment will utilize components of the Drain, which were originally designed solely for the transport and storage of drainage water. Specifically, it will be demonstrated that with certain modifications, the Drain, itself, can be used as a partial treatment unit with nutrient removals of up to 40 to 50 percent, and that with similar modifications, the Drain up to Kesterson, together with the proposed Kesterson storage reservoir, can accomplish up to 100 percent nutrient removal.

Basic Assumptions. The Drain, as planned, will promote a degree of algal growth regardless of design and use which will result in

¹ Assistant Civil Engineer, California Department of Water Resources, Fresno, California; Research Aquatic Biologist, Federal Water Pollution Control Administration, Fresno, California; Professor of Sanitary Engineering and Public Health, University of California, Berkeley, California; and Senior Sanitary Engineer, California Department of Water Resources, Fresno, California, respectively.

incorporation of soluble nutrients into cells and the resultant reduction of soluble nutrients, which will necessitate some form of algae separation before terminal discharge into the Bay-Delta waters.

The San Luis Drain, as it is now proposed, has a surface area of approximately 770 acres and with the expected flow will have a mean detention time of 6.3 days. Based on these considerations, it is highly likely that the Drain will support an undetermined but possibly significant algal growth at the point of discharge into the Delta, depending on time of year. This growth will occur naturally due to the high level of nutrients that are present in the drainage waters, together with the prevailing environmental conditions (sunlight and temperature) that are present in the San Joaquin Valley from early spring through late fall. Growth may take one or both of two forms; sessile algae growing on the canal walls in the photic zone, or suspended algae growing in the photic zone but uniformly distributed in the cross-section of the flow.

Unless specifically removed, it is likely that suspended algae will pass unaltered through any subsequent process, while sessile algae will break off the walls in clumps, which will then clog any filtration process.

Since algal growth in the Drain will be unavoidable, maximization of this growth, followed by complete separation of the algal biomass, will result in the following benefits:

- a. Land requirements for the treatment facility will be reduced in proportion to the degree of induced algal growth in the Drain. Thus, the principal cost for treatment will be reduced.
- b. The Drain will be put to a dual use--concurrent transport and treatment of drainage water.
- c. The velocity of the Drain is great enough to provide a degree of turbulence, which will meet part or all of the mixing requirements necessary to promote the optimum algal growth desired; power requirements for this growth will be reduced, thus reflecting still another cost reduction.

Kesterson Reservoir, as originally envisioned, was to act as a storage reservoir to hold the first 2 years of drainage flows from the San Luis Drain (from December 1969 to December 1971), while the northernmost portion of the Drain from Kesterson to Antioch was being constructed. With an estimated annual inflow to the San Luis Drain during these years of approximately 2,500 acre-feet, the

reservoir will store 5,000 acre-feet of water. Based upon a proposed 3-foot depth, the reservoir will initially encompass a land area of about 1,700 acres. Eventually the land area of the reservoir would be built up to about 3,000 acres to serve a variety of uses.

At the time the northern section of the Drain is completed and Kesterson Reservoir is emptied of the 2 years' storage, it is possible that a substantial growth of algae will have formed in the reservoir which will further increase the amount of algae to be found in the Drain. It is not unrealistic to foresee an algal concentration of up to approximately 100 mg/l or more in the Drain at Antioch during the period the reservoir is being emptied. Based upon light considerations only, the depth of the Drain at Antioch will limit the maximum concentration of algae that can be supported there to 100 mg/l (see calculations in Appendix).

Current Status of Treatment Processes. Research has been underway at Firebaugh for over 2 years to determine the feasibility of removing nitrogen from agricultural drainage water by either algae stripping, anaerobic denitrification in either deep ponds or filters, or a combination of both.

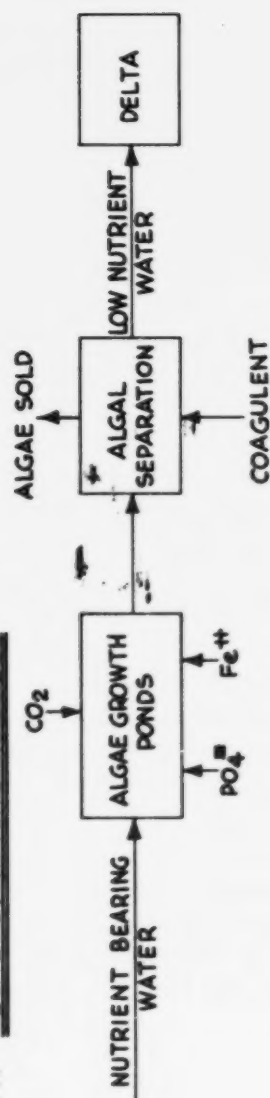
The anaerobic filters have demonstrated a high efficiency during most of the year but appear to be sensitive to temperatures below 12°C. and experience problems of clogging after prolonged operation.

The algae stripping process during the course of the 2 years of research has shown a steady improvement in efficiency, due in part to algal adaptation, but also due to increased knowledge of the properties of the process by those conducting the studies. It has also been shown that over 95 percent of the algal cells can be separated from the liquid effluent through coagulation with small quantities of lime or alum, followed by sedimentation.

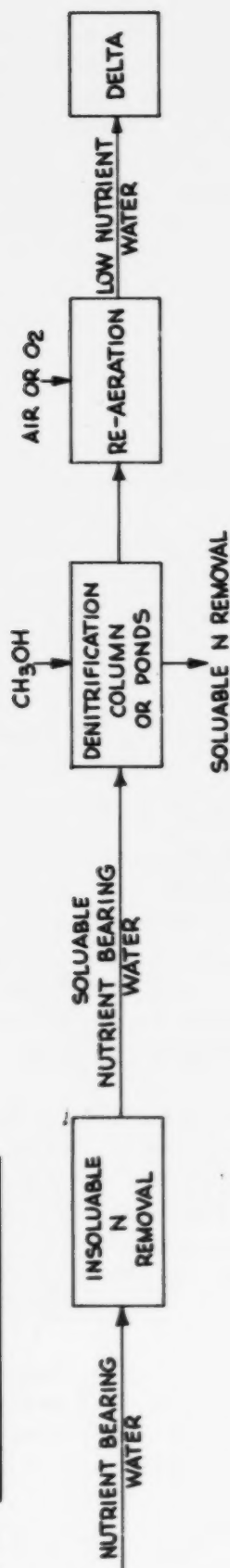
Thus, both processes appear to be technically feasible, and one can envision the types of systems in which they would be used. For example, several candidate systems are shown in figures 1-A, 1-B, and 1-C. A combined process (figure 1-C) in which algae are grown and removed prior to column denitrification would give the greatest factor of safety at approximately the same cost as either of the two separate processes (figures 1-A and 1-B).

Effect of In-Line Treatment on Overall Cost of Different Proposed Treatment Processes. Algae Stripping Process--An acceleration of the treatment process through the provision of a high initial biomass (the algae grown in the Drain) with a reduction in the soluble nutrient level will decrease costs by:

I-A ALGAE STRIPPING PROCESS



I-B COLUMN DENITRIFICATION



I-C COMBINED ALGAE STRIPPING - COLUMN DENITRIFICATION PROCESS

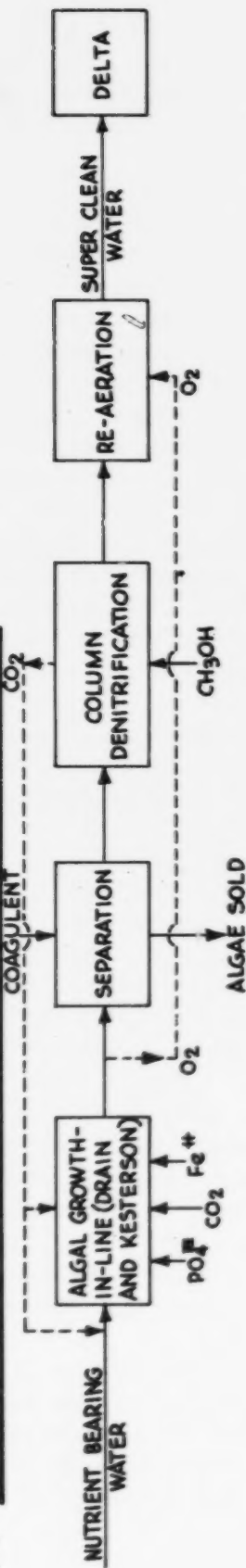


Fig. 1. SYSTEM DIAGRAM CANDIDATE PROCESSES FOR NUTRIENT REMOVAL

- a. Reducing the land requirements for a treatment plant.
- b. Reducing the construction costs of the plant.
- c. Reducing power and maintenance costs for a treatment plant.

Anaerobic Denitrification Filters--As noted previously, it will be difficult, if not impossible, to eliminate endemic algal growth from the Drain under existing nutrient and light conditions. Any nitrogen incorporated into algal cells in transit will be unavailable for treatment by denitrification, if the cells pass through the filter. This nitrogen will then be discharged to the Delta and eventually could be regenerated as soluble nitrogen. If the cells remain in the filter, then a further problem of filter clogging will arise. Research currently in progress at Firebaugh to determine what effect algal-laden water will have on the filters indicates that it adversely affects filter performance by increasing the concentration of soluble nitrogen in the filter effluent.

Thus, if algal growth in the Drain could be optimized and the resulting algae separated prior to filter treatment, the unit cost of treatment (which includes separation) could be reduced in the following ways:

- a. The total area requirements for terminal treatment will be reduced approximately in proportion to the reduction in soluble nutrients (principally nitrate-nitrogen). The land area required for separation facilities will be small compared to the reduction in land area required for the filters.
- b. Filter construction costs will similarly be reduced.
- c. Methanol costs will be reduced in proportion to the amount of nitrate-nitrogen removed by In-Line Treatment.
- d. Power and maintenance costs will similarly be reduced.

Suggested Modifications to Improve In-Line Treatment

As previously stated, the Drain without modification has the potential for reducing nitrogen levels by a significant amount. Similarly, Kesterson Reservoir outflow will increase the algae concentration in the Drain by as much as 100 mg/l. Therefore, any modification to the Drain which enhances this efficiency will have significant economic value, when compared to the original estimate for treating Drain water solely in a terminal plant. A number of different alternatives to the original algae stripping proposal thus becomes apparent. These are as follows:

Enhance Algal Growth in the Drain by Seeding and Nutrient Addition (If Required). It will be necessary to seed the Drain at Kettleman City with approximately 50 mg/l of algae in order to produce 100 mg/l of algae at Antioch (see Appendix). Work at the Firebaugh Treatment Center has indicated that the Alamitos Sump water is deficient in carbon, phosphorus and iron; three nutrients required to support an algal growth capable of high nitrogen uptake. In order to promote algal growth at Firebaugh, it has been necessary to add small quantities of these three ingredients to the sump water. If a similar nutrient limitation is present in the combined drainage waters feeding the San Luis Drain, then nutrient addition would be required along with the initial seeding. However, it should be pointed out that the Alamitos Sump water is fed by an isolated tile drainage system. The fact that the San Luis Drain will be fed by numerous drainage systems in the San Joaquin Valley greatly reduces the prospect that the composite drainage water will be lacking in either iron or phosphorus. Carbon is available to the algae only in the form of carbon dioxide or its derivative, the bicarbonate ion. Work at Firebaugh has indicated that there appears to be a seasonal change in the CO₂ requirements necessary for high nitrogen conversion into algal cellular material. Thus, it is possible that supplementary CO₂ will not be required or may be required only during a portion of the year and during several hours of the day.

Seeding of the Drain could be accomplished by maintaining a growth pond at Kettleman City which would feed into the Drain. It is estimated that a 1,000-acre pond will be necessary to produce the required 50 mg/l initially in the Drain.

Thus, it would be possible to reduce soluble nitrate-nitrogen levels at Antioch by up to 40 percent by using the Drain as it is presently designed with seeding and nutrient additions (if required). Land requirements and construction costs for a treatment plant would be similarly reduced by 40 percent.

Keep the Drain Essentially as Proposed but Include Kesterson Reservoir as a Permanent Part of the Flow-Through System. If Kesterson Reservoir were a permanent part of the Drain System with a detention time of 10 days at peak flow (at a 3-foot depth), then it would be possible to produce 100 mg/l of algae in the reservoir effluent, thus eliminating the need for initial seeding. Nutrient addition may be required in accordance with the previous discussion. As in the first proposal soluble nitrate-nitrogen levels at Antioch would be reduced 40 to 50 percent with a corresponding savings in the cost of treatment.

Modify and Use All or Part of the Drain for Partial Treatment.

Assuming nutrients are not limiting, the growth of algae is primarily dependent on the quantity of available light energy. In an outdoor system, sunlight is the sole source of this energy. Thus, the quantity of energy available for the photosynthetic process is directly proportional to the amount of surface area exposed to sunlight.

With regard to using the Drain as an algal growth system, any method that will increase the effective surface area of the Drain will increase the photosynthetic efficiency and improve the treatment process.

Several obvious ways to increase this effective surface area include:

Increase the Surface Area of the Drain--Ideally, in order to accelerate the growth of algae in the Drain, itself, the entire Drain should be constructed so as to optimize surface area and minimize depth. In order for the Drain to act as a sole treatment unit, its surface area would have to be increased sevenfold over the current design. Since no recommendations have been made concerning choice of nutrient removal process at this time, and because the Drain up to Dos Palos has already been designed, there does not appear to be any justification for further consideration of widening the Drain.

Hydraulically Modify the Drain to Create Turbulence--A direct relationship exists between the degree of turbulence and effective surface area. By utilizing the flow of the Drain for mixing and hydraulically modifying the Drain to create turbulence, the overall photosynthetic efficiency of In-Line treatment can be greatly improved.

Modifications to be considered are:

- a. Baffles along the bottom and/or sides to create turbulence (at the projected velocities).
- b. Drop structures strategically along the length of the Drain (at the projected velocities).
- c. Aeration with air (or CO₂ enriched air) to create turbulence; aeration could be effected as in an aeration tank of an activated sludge plant. Aeration units could similarly be located strategically along the length of the Drain.
- d. Pumps at intervals along the Drain to promote turbulence.

However, without further investigation, it is difficult, if not impossible, to quantitatively predict what degree of turbulence is required to produce a desired algal concentration.

Kesterson Reservoir as a Combined Storage Reservoir-Treatment Plant.

Essentially, a major portion of the San Luis drainage flow and the bulk of the nitrogen load will enter the Drain before Kesterson Reservoir. Since the land for Kesterson Reservoir (on the order of 3,000 to 6,000 acres) has already been selected as a large part of the overall drainage system, the concept of converting Kesterson Reservoir into a combined storage reservoir and treatment plant appears to be most promising.

By converting the reservoir into an algal growth system with operating depths varying from 1 foot to 3 feet, the system has the capability for over 90 percent treatment and still has the flexibility for acting as an emergency storage reservoir.

Studies at Firebaugh, thus far, indicate that some degree of mixing is required in algal systems for optimum growth and nutrient removal. Research to date indicates several hours of mixing per day appears adequate although research involving shorter mixing periods, which also appears favorable, is continuing in this area; but, regardless of the degree of mixing, it will be a consideration in determining operational costs for a treatment plant.

From the start of this project, mixing was recognized as a major operational factor in the algae stripping process and, as a result, several proposals have been brought forth as how to best accomplish this objective. It has been suggested that pumps might be centralized in turret fashion to serve several series of ponds to minimize operational costs or that pumps could be installed in a racetrack-type pond, such as at Firebaugh. Any treatment plant utilizing these types of mixing systems will require substantial amounts of power which will directly affect the total processing costs.

The system proposed for combining the reservoir for storage and treatment would minimize the power required for mixing by either a complete gravity or combined initial pumping-gravity flow system. The land of Kesterson Reservoir embodies a natural slope to the north. Thus, a minimum amount of cut and fill would be required to produce a slope of the required degree. Excavated earth could then be efficiently used for side slopes. If necessary, low cost pumping could be used initially to produce the necessary velocities in the treatment process.

A design of such a treatment facility, which lends itself very effectively to the dual use proposed, entails a series of equally spaced

channels running longitudinally along the length of the reservoir. Figure 2 is a sketch of such a proposed plant. The channels would follow the natural slope and the flow through each channel could be regulated by individual head gates. Similarly, these gates could isolate each channel for treatment flexibility and/or maintenance.

Any desired detention time could be maintained by recirculating a portion of the effluent. This design will have the following inherent advantages over a terminal treatment plant as originally envisioned:

- a. Greatly reduces construction costs due to the simplicity of design.
- b. Provides a great degree of flexibility of operation--can adjust to seasonal variations in flows.
- c. Minimizes power requirements by using gravity for a part of the required mixing.
- d. Prevents biomass buildup by eliminating stagnant areas that are often present in ponds of the Firebaugh design.
- e. Allows for cyclic removal, if required.
- f. Treatment can still be carried on while the system is being used as a reservoir.
- g. When the Master Drain is put into operation, the reservoir can be expanded to meet future treatment requirements (see sketch).

The first stage of Kesterson Reservoir has already been designed and encompasses a series of 12 ponds, each 3 to 4 feet deep. The total land area involved is in the order of 1,300 acres. There still remains 3,000 to 4,000 acres of land which can be utilized for the combined algal growth system and storage reservoir. Figure 3 is a location map of the proposed Kesterson Reservoir and shows the portion already designed, together with the land area available for future reservoir use. Figure 4 is a site plan of the system, showing how an algal system, as envisioned in figure 2, could be incorporated into the land area reserved for the remainder of the reservoir.

If the size of the reservoir were 4,000 acres, together with the 1,300 acres for the first stage reservoir, then up to 90 percent of the influent nitrogen from the San Luis Drain waters could be incorporated into algal cell material (see Appendix for calculations). Perhaps the most significant aspect of using Kesterson Reservoir as

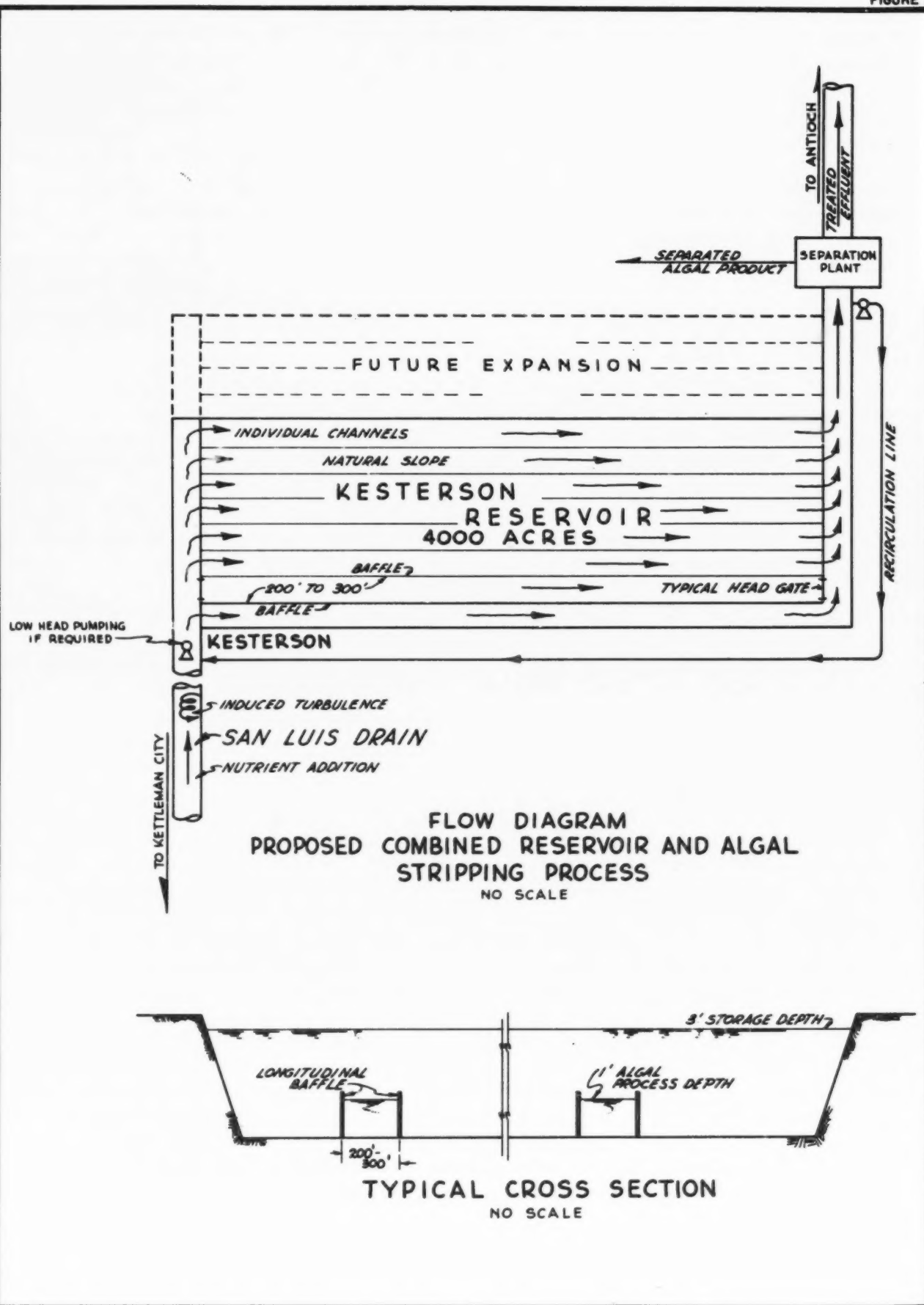


FIGURE 3



Table 1 - In-Line Treatment
Savings in Land Costs as
Compared to Terminal Treatment Facility

Proposal	Nitrogen Removal Expected (percent)	Land Area Saved* Through Reduction in Land Required for Terminal Treatment Plant (acres)	Estimated Savings**** In Cost Through Re- duction in Additional Land Required (\$ x 10 ⁶)
A - Enhance algae growth in Drain	40	2,320	4.64
B - Include Kesterson Reservoir to flow through system	40	2,320	4.64
C - Modify and use all or part of Drain for treatment	50-75**	2,400-4,350	5.8-8.7
D - Convert Kesterson Reservoir to combined system	90	5,800	11.6
E - Combine two processes in series-type operation	up to 100	5,800 ***	11.6

* Land area required for 90 percent treatment by algae stripping process equals 5,800 acres.

** Rough estimate.

*** Does not include area required for filters.

**** Based on \$2,000/acre in Antioch area.

a treatment unit is that it has the potential for future conversion into a stripping plant, if it were necessary to delay installing any treatment process until some time after construction of the entire Drain, including the reservoir. No additional land would be required for such a process, resulting in a very significant savings in cost.

Similarly, the system may be expanded conveniently as the flow in the Drain increases. Thus, it would be possible to build the treatment plant in stages concurrent with those to increase the storage capacity of the reservoir.

Combine the Algae Stripping Process and the Anaerobic Filters in Series. Inasmuch as the studies at Firebaugh indicate that both the anaerobic filters and the algae stripping process are technically feasible, the concept of combining the two systems in a series-type operation (see figure 1-C) merits intensive investigation. Kesterson Reservoir, as outlined in the previous section, could serve as the site for the algae stripping process, followed by algal separation facilities, and then followed by the anaerobic filters for final treatment. A significant aspect of this design is that it inherently embodies a substantial factor of safety and insures a polished drainage water virtually free of nitrogen and other nutrients even under extreme circumstances.

If a dependable market can be found for the harvested algae, it is reasonable to assume that a substantial fraction of the cost of the entire treatment facility can be defrayed. The whole system could be easily expanded to meet future needs.

Table 1 gives a gross estimate of both land and cost savings that could be achieved by In-Line Treatment. As can be seen from this table, a savings of approximately \$11 to \$12 million is possible when in-line treatment is used for 90 to 100 percent nitrogen removal as compared to terminal treatment facility as originally envisioned.

Summary

Work at Firebaugh has demonstrated that it is possible to remove nitrogen from drainage water by either algae stripping or anaerobic denitrification.

It has been suggested in this proposal that serious consideration be given to In-Line Treatment as both an economical and practical method for nutrient removal.

Because Kesterson Reservoir is an integral part of the proposed drainage system and contains the required area needed for treatment by algae stripping, it seems logical to use it as a dual-purpose treatment and storage reservoir.

Kesterson Reservoir, if modified as suggested, has the potential to provide nitrogen removals in excess of 90 percent.

The Drain, itself, has the capability for partial treatment. Although it may be impractical to physically modify the dimensions of the Drain for enhancing algal growth, it is possible to use the Drain for this purpose by creating turbulence, adding nutrients, and by seeding.

Work at Firebaugh has demonstrated that it is technically feasible to remove nitrogen by growing and harvesting algae. However, at this time, there are many unanswered questions about the process. Some of the more important problems to be solved include:

a. What are the optimum nutrient conditions required for maximizing nitrogen removal?

b. What is the optimum detention time?

c. What is the maximum depth under which the process will work? For design purposes in this report, a depth of 1 foot has been used. This depth has been found to be adequate for maximum nitrogen removal at Firebaugh. However, there are some indications that greater depths will be as efficient. If this holds true, then this proposal for In-Line Treatment will be conservative in its estimates of land required.

d. What degree and duration of mixing is required?

The combining of the algae stripping process with the anaerobic filters in a series operation at Kesterson Reservoir would insure an efficient system under the most extreme circumstances and would provide the maximum operational flexibility.

It appears from this brief preliminary analysis of the situation that the use of In-Line Treatment can reduce treatment costs considerably.

Recommendations

Based on the analysis contained herein, it is strongly recommended that a more comprehensive analysis of the use of In-Line Treatment be made in the near future. This analysis should include actual design of an In-Line Treatment unit with estimates of construction costs of In-Line Treatment, estimated operational costs, and, inasmuch as algal treatment is dependent on defraying the overall cost through economic recovery of the value of algae, further detailed investigation for finding an economic market for the algae byproduct.

APPENDIX

A. Detention Time in San Luis Drain

Characteristics of Drain

Segment	Length (miles)	Flow Capacity (cfs)	Bottom Width (ft)	Depth (ft)	Cross* Sectional Volume		Deten- tion Time (days)
					Area (ft ²)	ft ³ x10 ⁶	
Kettleman City to Highway 198	12	100	6.0	5.5	78.4	4.97	0.577
Highway 198 to Jameson Ave.	15	150	7.0	6.4	106.1	8.42	0.650
Jameson Avenue to Lassen Ave.	7	200	7.0	7.3	131.2	4.87	0.281
Lassen Avenue to Tranquillity	17	300	8.0	8.0	160.0	14.4	0.556
Tranquillity to Kesterson	62**	300	8.0	8.0	160.0	43.9	1.695
Russell to Ness Avenue	10	300	8.0	5.8	96.9	5.06	0.195
Kesterson to Antioch	75	450	10	9.7	237***	93.2	2.410

TOTAL DETENTION TIME = 6.364

* All side slopes 1.5:1

** Russell to Ness Avenue is included in the Tranquillity to Kesterson segment.

*** Not available if treatment is carried out at Kesterson.

B. Maximum Algal Growth Possible in Drain Under Natural Conditions

The San Luis Drain has a surface area of 770 acres and a mean detention time of 6.3 days. If 1 mg/l of algae were initially presented in the Drain, and assuming an average of four cell doublings during transit to the Delta, then 16 mg/l of algae would be present at discharge. However, consideration must be made of the fact that if even 2 mg/l of algae were present initially and the same number of doublings occurred, then the Drain would contain 32 mg/l of algae. One more doubling would bring the level of algae to 64 mg/l.

Therefore, it is almost impossible to predict the amount of algae which the Drain will contain both initially and at discharge into the Delta. It should be recognized, however, that the Drain does have the potential for supporting a relatively high concentration of algae and that consideration of this fact should enter the design of any nutrient removal process.

C. Amount of Nitrogen Removed From Drainage Water By Naturally Occurring Algae

Assumptions

- a. Algae concentration at discharge = 16 to 65 mg/l. (Estimate)
- b. Nitrogen content of algal cells = 8-10 percent (use 8 percent)
- c. Total nitrogen concentration in drainage water = 20-25 mg/l (use 25 mg/l).
- d. Therefore,

amount of nitrogen removed from drainage water and converted into algal cell material is:

$$16 \text{ mg/l} \times 0.08 = 1.28 \text{ mg/l (minimum estimate)}$$

$$64 \text{ mg/l} \times 0.08 = 5.12 \text{ mg/l (maximum estimate)}$$

or approximately:

$$\frac{1.28}{25} \times 100 = 5 \text{ percent (minimum estimate)}$$

$$\frac{5.12}{25} \times 100 = 20 \text{ percent (maximum estimate)}$$

of the incoming nitrogen will be removed.

D. Amount of Algae Theoretically Possible in Outflow From Kesterson Reservoir

Assumptions

- a. Maximum flow in San Luis Drain = 290 MGD
- b. Surface area of Kesterson Reservoir = 3,000 acres
- c. Depth of reservoir = 3 feet (normal operating depth).

$$\text{Detention Time} = \frac{3,000 \times 43,560 \times 3 \times 7.48}{290 \times 10^6} = 10 \text{ Days}$$

Assume that in April and September conditions are critical

$$\text{Average solar energy during these months} = 8 \times 10^6 \text{ K cal/acre/day.}$$

$$\text{Total energy/reservoir/day} = 3,000 \times 8 \times 10^6 = 24 \times 10^9 \text{ K cal.}$$

Assume that photosynthetic efficiency in converting solar energy to algal biomass = 3 percent

Algae contain 6 K cal/gram (average value)

Therefore, amount of algae produced per day in pond equals

$$\frac{24 \times 10^9 \times 3 \times 10^{-2}}{6} = 12 \times 10^7 \text{ grams}$$

Average algal concentration in outflow from Kesterson Reservoir =

$$\frac{12 \times 10^{10} \text{ mg}}{290 \times 10^6 \times 3.79} \approx 100 \text{ mg/l}$$

Based upon calculations in part F of the Appendix, the Drain at Antioch has the capability for supporting approximately 100 mg/l of algae based upon light limitations only. Therefore, it is possible that 100 mg/l of algae leaving Kesterson Reservoir will still be present at Antioch, the point of discharge to the Delta.

E. Nitrogen Conversion To Algal Cells in Kesterson Reservoir When Used as a Treatment Unit

a. Nitrogen removal in First-Stage Storage Reservoir

Area = 1,300 acres

Depth = 3 feet

Flow Rate = 290 MGD

$$\text{Detention Time} = \frac{1,300 \times 43,560 \times 3 \times 7.48}{290 \times 10^6} = 4.3 \text{ days}$$

Same assumptions for solar energy conversion into algal biomass as in Part D.

Therefore, amount of algae produced per day in pond equals:

$$\frac{(1.3 \times 10^3) (8 \times 10^6) (3 \times 10^{-2})}{6} = 5.2 \times 10^7 \text{ grams}$$

Average algal concentration in outflow from First-Stage Reservoir equals

$$\frac{5.2 \times 10^{10} \text{ mg}}{290 \times 10^6 \times 3.79} = 47 \text{ mg/l}$$

b. Nitrogen Conversion to Algal Cells in Combined Treatment Plant-Storage Reservoir

Area = 4,000 acres
Depth = 1 foot
Flow Rate = 290 MGD

$$\text{Detention Time} = \frac{4,000 \times 43,560 \times 1 \times 7.48}{290 \times 10^6} = 4.5 \text{ Days}$$

$$\text{Total energy/reservoir/day} = 4,000 \times 8 \times 10^6 = 32 \times 10^9 \text{ K Cal}$$

Assume that photosynthetic efficiency in converting solar energy to algal biomass = 5 percent (5 percent could be obtained due to excellent hydraulic design of reservoir and greater depth).

Amount of algae produced per day in pond equals

$$\frac{32 \times 10^9 \times 5 \times 10^{-2}}{6} = 26.7 \times 10^7 \text{ grams}$$

Average algal concentration in outflow from Treatment Plant =

$$\frac{26.7 \times 10^{10} \text{ mg}}{290 \times 10^6 \times 3.79} = 243 \text{ mg/l}$$

$$\text{Total algae produced in Kesterson Reservoir} = \frac{243 + 47}{290 \text{ mg/l}}$$

Assume: Nitrogen content of algal cells = 8 percent.

Influent nitrogen content = 25 mg/l.

Thus,

$$\text{Total Nitrogen in Algal Cells} = \frac{290 \times .08}{25} \times 100 = 93 \text{ percent}$$

F. Algal Growth Required For 90 Percent Nitrogen Removal

Algal cell material has an energy content of 6 K cal/gram or
 $6 \times 454 = 2,724$ K cal/lb. (dry weight) See attached Characteristics of the San Luis Drain (page 180).

Sunlight Energy Input:

To compute solar energy flux (S) input to surface of Drain
(Assume critical conditions in April and September); therefore,

$$\text{Daily Energy Input (S)} = 2 \times 10^2 \text{ cal/cm}^2/\text{day}$$

$$\text{and, energy to 1 acre} = 2 \times 10^2 \times 4,025 \times 10^7 \times 10^{-3} \\ \text{K cal/cal} = 8 \times 10^6 \text{ K cal/acre/day}$$

Necessary Energy Output - Entire Drain

450 sec. ft. = 290 million gallons per day

Nitrogen content of drainage water = 25 mg/liter (maximum)

Assume 90 percent removal; therefore, there will be 22.5 mg/liter in algal cells.

Algal biomass to be produced at 50 percent protein =
 $50/6.25 = 8$ percent N. therefore, biomass to be produced
 $= 22.5/.08 = 280$ mg/liter.

Therefore, final algal concentration should be 280 mg/liter,
and the corresponding required biomass production per day is
 $280 \times 8.34 \times 290 = 675,000$ lbs. per day.

G. What Can Be Done To Grow Algae in The Drain

In order to use the Drain most strategically as a growth unit, it will be necessary to seed the Drain with a concentration of algae sufficient to give complete light absorption initially and to permit as many doublings as possible to occur during transit. With good mixing, doubling will start at once and may continue up to a concentration permitting 1/3 d light transmission.

In this case the Drain would be initially seeded with a concentration proportional to the mean depth at Kettleman which is 3.77 ft.

$$d = 3.77 \times 30.48 = 115 \text{ cm}$$

Using the Beer-Lambert equation for concentration as a function of depth, the concentration of algae at Kettleman should be:

$$C_c = \frac{9}{115 \times 1.5 \times 10^{-3}} \approx 52 \text{ mg/liter}$$

and at the end of the 6.3-day transit the concentration would be

$$d = 6.15 \times 30.48 = 188 \text{ cm (Depth at Antioch)}$$

$$C_c = \frac{9}{188 \times 1.5 \times 10^{-3}} \times 3 \approx 100 \text{ mg/liter}$$

Antioch concentration will be light limited at 100 mg/liter and to attain any further increment shallow ponding would be required.

The increment of 48 mg/liter between Kettleman and Antioch would constitute fixation of $48 \times 290 \times 8.34 \times 2,724 =$

310×10^6 K cal of solar energy in the form of algae or

$$\frac{310 \times 10^6}{7.67 \times 10^2} = 40.4 \times 10^4 \text{ K cal/acre/day}$$

The mean conversion efficiency would be

$$\frac{40.4 \times 10^4}{8 \times 10^6} \times 100 = 5.06 \text{ percent. } 5.06 \text{ percent conversion}$$

efficiency is higher than the anticipated efficiency of 3.5 percent in the originally planned 5,800 acres of 12-inch-deep ponds. However, a 5.06 percent conversion efficiency may be possible because of the greater depth and light absorption and the excellent mixing provided in the Drain if it has a velocity of 2 feet per second. The 767-acre Drain, itself, thus would be equivalent to roughly 1,000 acres of regular growth ponds at Antioch.

H. How Could the Drain Be Best Used to Accomplish the Above?

The strategy would be as follows:

Grow algae at Kettleman City and seed the Drain with about 52 mg per liter dry weight basis.

Required acreage at Kettleman City about	1,000
Acreage equivalent of Drain	<u>1,000</u>
Total land in seeding and conveyance	2,000
Balance of land required at north end	
5,800 - 2,000 =	3,800 acres

As one may see, a substantial savings in total land as well as a savings in expensive "north end" land could result from this scheme.

Inasmuch as land in the vicinity of Kesterson is probably much less expensive than land in the vicinity of Antioch, and because there is to be a pond there anyway, it might be worthwhile to consider operating a major growth and harvesting facility at Kesterson. This could possibly reduce the land requirement in the vicinity of Antioch to about 1,500 acres, or less.